

[54] **AZO FREE RADICAL INITIATORS  
CONTAINING ULTRAVIOLET LIGHT  
STABILIZING GROUPS**

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[21] **Appl. No.: 680,545**

[22] **Filed: Apr. 27, 1976**

**Related U.S. Application Data**

[60] **Continuation-in-part of Ser. No. 435,622, Jan. 22, 1974,  
abandoned, which is a division of Ser. No. 98,893, Dec.  
16, 1970, abandoned.**

[51] **Int. Cl.<sup>2</sup> ..... C08F 4/04; C08F 4/34;  
C08F 12/08**

[52] **U.S. Cl. .... 526/208; 260/75 T;  
260/145 A; 260/192; 260/308 B; 260/429.7;  
260/448.2 R; 260/934; 526/183; 526/193;  
526/194; 526/198; 526/204; 526/213; 526/215;  
526/216; 526/346**

[58] **Field of Search ..... 526/208, 204, 209, 210,  
526/213, 214, 219, 346**

[56] **References Cited**

**U.S. PATENT DOCUMENTS**

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*Primary Examiner*—Christopher A. Henderson

[57] **ABSTRACT**

Compounds which contain azo or peroxide linkages as well as the radical of an ultraviolet light stabilizing group are described. These compounds function as polymerization initiators which cause an ultraviolet light stabilization group to be chemically bound to the polymer.

**4 Claims, No Drawings**

### AZO FREE RADICAL INITIATORS CONTAINING ULTRAVIOLET LIGHT STABILIZING GROUPS

This application is a continuation-in-part of application Ser. No. 435,622, filed Jan. 22, 1974, now abandoned, which in turn is a division of application Ser. No. 98,893, filed Dec. 16, 1970, now abandoned.

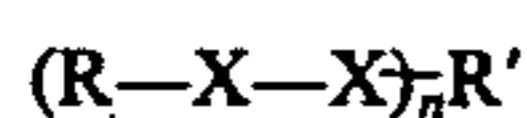
This invention relates to novel compounds which are free radical initiators as well as being ultraviolet light stabilizers.

It is well known that many ethylenically unsaturated monomers are polymerized by the use of free radical initiators, i.e. those having aliphatic azo or peroxide groups. It is also well known that many of the polymers resulting from the polymerization of such monomers are subject to degradation by ultraviolet light, and therefore require the presence of an ultraviolet light stabilizer to extend the useful life of such polymers. Normally, such stabilizers are added to the polymer by methods such as milling or other methods of physical mixing. In more recent times techniques of copolymerization have been employed by means of which unsaturated derivatives of certain ultraviolet light stabilizing compounds have been copolymerized with vinyl monomers to form a light stabilized polymer. The method of physically mixing the stabilizer and the polymer has always been unsatisfactory because the resulting two-phase system is incompatible. The stabilizing compound inevitably migrates to the surface of the polymer and becomes separated from the polymer by evaporation, leaching, or erosion.

The copolymerization technique is much more satisfactory than physically blending because it provides a chemically bound stabilizer which is not removed by physical processes. This method, however, has many inherent disadvantages due to the chemical equilibria involved in copolymerization reactions. The comonomer providing the stabilizer component must have its reactivity balanced against that of the principal comonomer and the concentrations of these two comonomers adjusted accordingly in order to produce a product having the desired amount of stabilizer. The copolymerization technique also normally produces a product having much more stabilizer incorporated into the polymer than is necessary, and this increases the cost of the final product markedly. Furthermore, many of the stabilizer comonomers have a tendency to homopolymerize rather than to copolymerize and thereby to result in a product lacking in homogeneity.

It is an object of the present invention to provide novel compounds which function both as a free radical initiator and as an ultraviolet light stabilizer. It is another object of this invention to provide a light stabilized polymer wherein the stabilizer is chemically bound to the polymer and is present in an economical and regulated amount. Still other objects will be apparent from the more detailed description of this invention which follows.

In accordance with this invention, there is provided a free radical initiator containing ultraviolet light stabilizing groups and having the formula:



wherein  $-X-X-$  is  $-O-O-$  or  $-N=N-$ , R and R' are the same or different radicals, at least one of which comprises an ultraviolet light stabilizing radical, and n is 1 to 4.

### PEROXIDES

In accordance with one preferred embodiment of this invention  $-X-X-$  is the peroxide group  $-O-O-$ .

When  $n=1$  in this embodiment R and R' are both selected from the group consisting of hydrogen, acyl of 2-20 carbon atoms, aroyl of 7-20 carbon atoms, t-alkyl of 4-12 carbon atoms, t-cycloalkyl of 4-12 carbon atoms, t-aralkyl of 9-15 carbon atoms, alkoxy-carbonyl of 2-20 carbon atoms, cycloalkoxy-carbonyl of 4-20 carbon atoms, carbamoyl, phenylcarbamoyl, alkylcarbamoyl of 2-13 carbon atoms, cycloalkylcarbamoyl of 4-13 carbon atoms,  $\alpha$ -hydroxyalkyl of 2-10 carbon atoms,  $\alpha$ -hydroxycycloalkyl of 3-10 carbon atoms,  $\alpha$ -hydroperoxyalkyl of 2-10 carbon atoms,  $\alpha$ -hydroperoxycycloalkyl of 3-10 carbon atoms, alkylsulfonyl of 4-20 carbon atoms, cycloalkylsulfonyl of 3-12 carbon atoms, t-(alkoxyalkyl) of 4-20 carbon atoms, t-(alkoxycycloalkyl) of 4° carbon atoms, and monovalent organomineral.

When  $n=2$  in this embodiment R may be any of the radicals listed above for the condition of  $n=1$ , and R' is selected from the group consisting of carbonyl, alkylidene of 2-20 carbon atoms, cycloalkylidene of 3-12 carbon atoms, di-t-alkylene of 6-20 carbon atoms, di-t-cycloalkylene of 6-20 carbon atoms, di-t-aralkylene of 12-20 carbon atoms, and divalent organomineral.

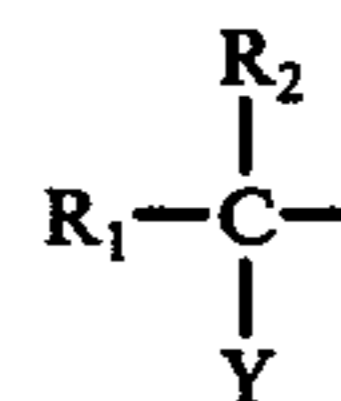
When  $n=3$  in this embodiment R may be any of the radicals listed above for the condition of  $n=1$ , and R' is selected from the group consisting of t-aralkyl-di-t-aralkylene of 15-20 carbon atoms, t-alkylalkylidene of 4-20 carbon atoms, t-cycloalkylalkylidene of 4-20 carbon atoms, t-alkylcycloalkylidene of 4-20 carbon atoms, t-cycloalkylcycloalkylidene of 6-20 carbon atoms, t-alkyl-di-t-alkylene of 10-19 carbon atoms, t-alkyl-di-t-cycloalkylene of 10-19 carbon atoms, t-cycloalkyl-di-t-alkylene of 10-19 carbon atoms, t-cycloalkyl-di-t-cycloalkylene of 10-19 carbon atoms, and trivalent organomineral.

When  $n=4$  in this embodiment R may be any of the radicals listed above for the condition of  $n=1$  and R' is dialkylidene of 5-16 carbon atoms. The mineral component in any of the organominerals mentioned above is selected from the group consisting of silicon, arsenic, antimony, phosphorus, germanium, boron, and tin.

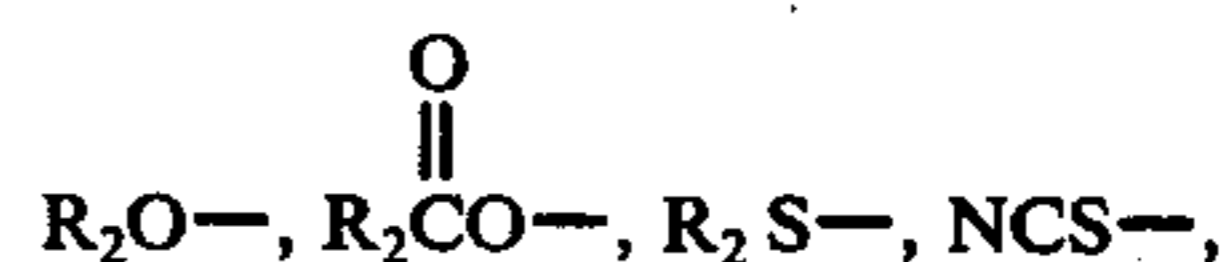
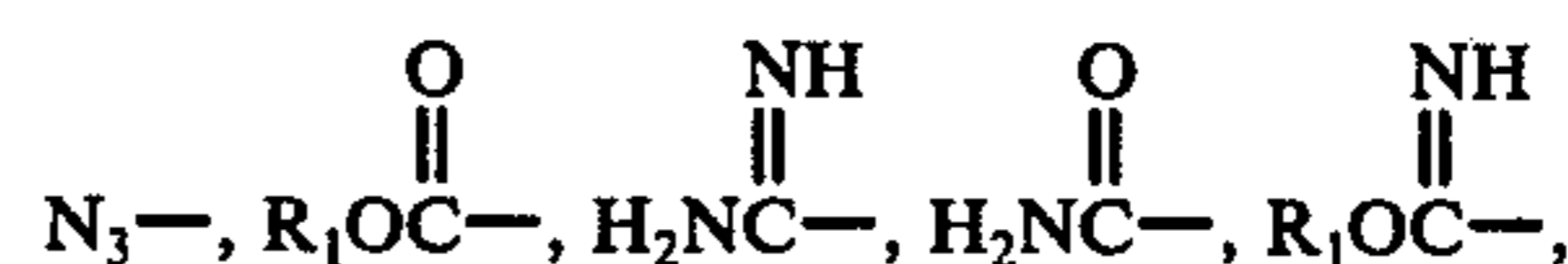
### AZO COMPOUNDS

In accordance with another preferred embodiment of this invention  $-X-X-$  is the azo group  $-N=N-$ .

When  $n=1$  in this embodiment R and R' are both selected from the group consisting of alkyl of 1-20 carbon atoms; cycloalkyl of 3-10 carbon atoms; aralkyl of 7-20 carbon atoms; and

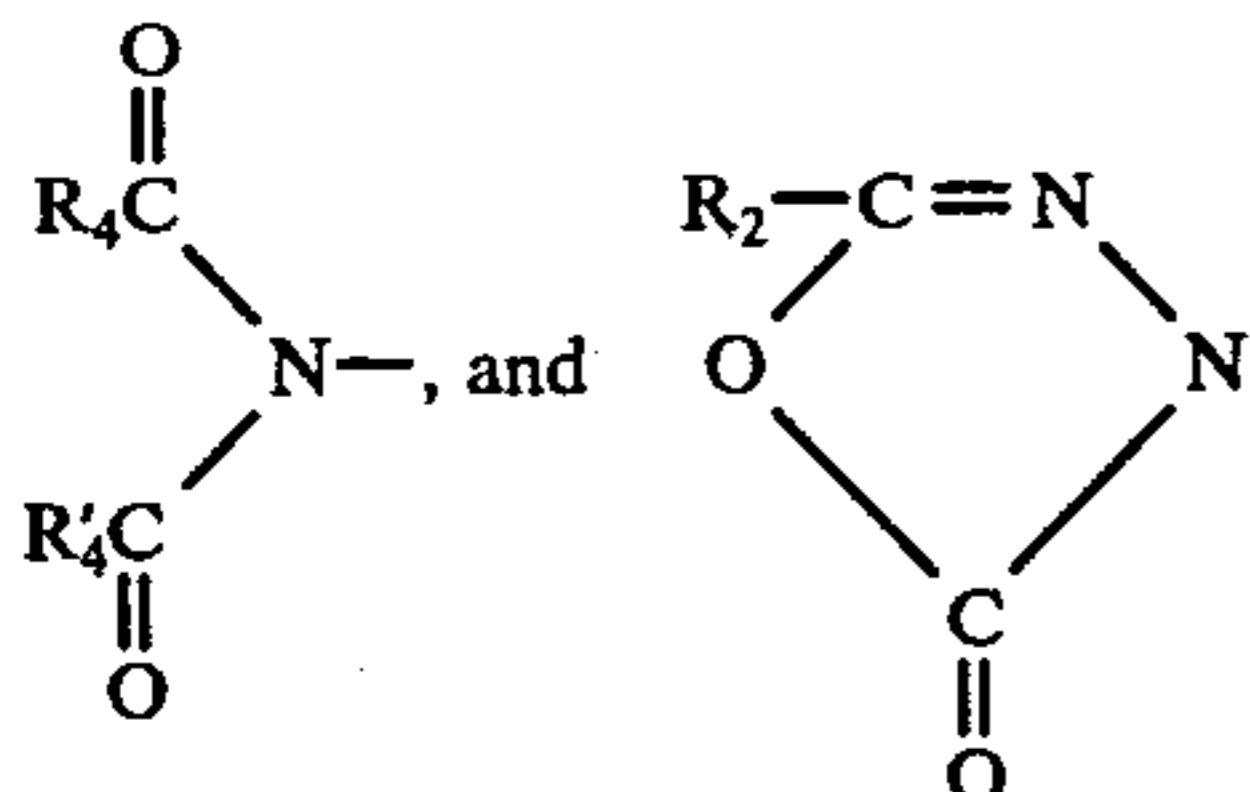
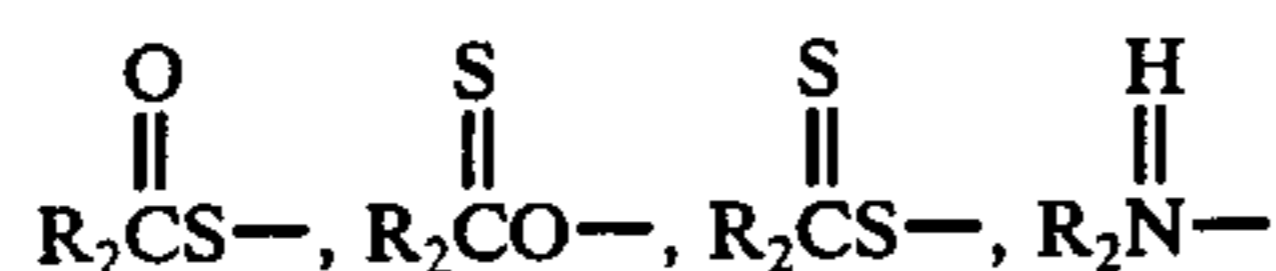
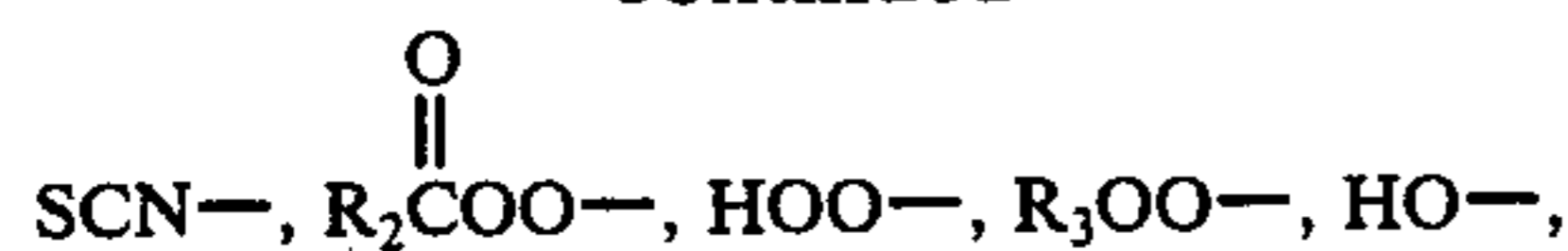


wherein Y is selected from the group consisting of  $NC-$ ,



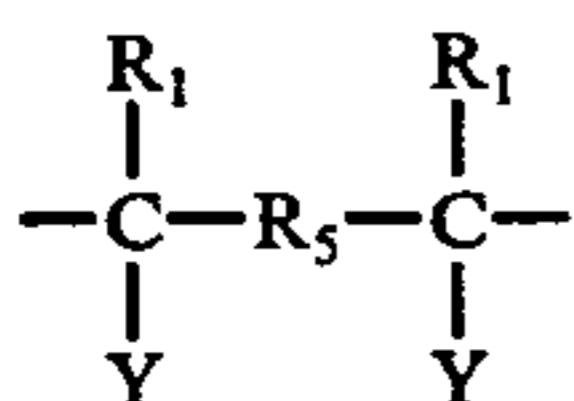
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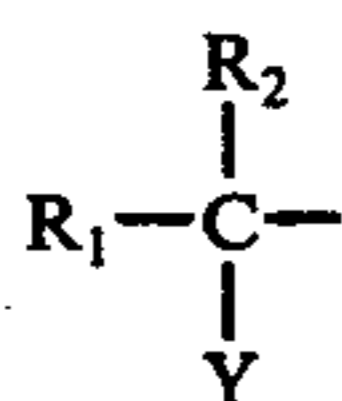


wherein  $R_1$  and  $R_2$  are selected from the group consisting of alkyl of 1–20 carbon atoms; cycloalkyl of 3–6 carbon atoms; alkylene of 2–30 carbon atoms when  $R_1$  and  $R_2$  are joined together; any of said alkyl, cycloalkyl, or alkylene containing as a substituent a member of the group consisting of carboxy, carboxy ester of 1–6 carbon atoms, hydroxy, and alkoxy of 1–6 carbon atoms; and wherein one but not both of  $R_1$  and  $R_2$  may in addition be phenyl, tolyl, xylyl, benzyl, or phenethyl;  $R_3$  is t-alkyl of 4–8 carbon atoms, t-cycloalkyl of 4–8 carbon atoms, or t-aralkyl of 9–15 carbon atoms;  $R_4$  and  $R_4'$  are alkyl of 1–6 carbon atoms, cycloalkyl of 3–6 carbon atoms, aryl of 6–12 carbon atoms when  $R_4$  and  $R_4'$  are not joined together, and alkylene of 1–6 carbon atoms or arylene of 6–12 carbon atoms when  $R_4$  and  $R_4'$  are joined together. Furthermore, with one exception,  $R$ , but not  $R'$ , may also be selected from the group consisting of aryl of 6–14 carbon atoms, acyl of 2–20 carbon atoms, aroyl of 7–20 carbon atoms, carbamoyl, alkylcarbamoyl of 2–7 carbon atoms, cycloalkylcarbamoyl of 4–11 carbon atoms,  $-\text{CO}_2\text{Na}$ ,  $-\text{CO}_2\text{K}$ , alkoxy-carbonyl of 2–7 carbon atoms, cycloalkoxy-carbonyl of 4–11 carbon atoms, and aryloxy-carbonyl of 7–13 carbon atoms. The one exception mentioned above is that when  $R$  is carbamoyl,  $R'$  can be, in addition, alkoxy-carbonyl of 2–7 carbon atoms, cycloalkoxy-carbonyl of 4–11 carbon atoms, or aryloxy-carbonyl of 7–13 carbon atoms.

When  $n=2$  in this embodiment  $R$  may be any of the radicals listed above for the condition of  $n=1$  and  $R'$  is selected from the group consisting of di-t-alkylene of 6–20 carbon atoms, di-t-cycloalkylene of 6–20 carbon atoms, di-t-aralkylene of 12–20 carbon atoms, and



where  $R_1$  and  $Y$  are as defined above and  $R_5$  is alkylene of 1–10 carbon atoms or cycloalkylene of 3–10 carbon atoms. Furthermore, in this embodiment when  $n=2$  and  $R$  is alkyl, cycloalkyl, aralkyl or



(as defined above with respect to the condition of  $n=1$ ),

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$R'$  can, in addition, be diacyl of 3–10 carbon atoms, diaroyl of 8–14 carbon atoms, arylene of 6–12 carbon atoms, or



where  $R_5$  is alkylene of 1–10 carbon atoms, cycloalkylene of 3–10 carbon atoms, or alkyleneoxyalkylene of 2–20 carbon atoms.

When  $n=3$  in this embodiment  $R$  may be any of the radicals listed above for the condition  $n=1$  and  $R'$  is selected from the group consisting of tert-aralkyl-di-tert-aralkylene of 15–20 carbon atoms, tert-alkyl-di-tert-alkylene of 10–19 carbon atoms, trialkoxycarbonyl of 6–20 carbon atoms, triazinyl, triacyl of 6–20 carbon atoms, and triaroyl of 9–20 carbon atoms.

When  $n=4$  in this embodiment  $R$  may be any of the radicals listed above for the condition  $n=1$  and  $R'$  is selected from the group consisting of tetraacyl of 9–20 carbon atoms and tetraaroyl of 9–20 carbon atoms.

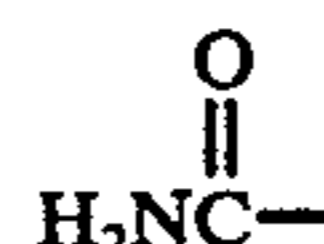
$R$  and  $R'$ , in any case, i.e. whether  $-\text{X}-\text{X}-$  is  $-\text{O}-\text{O}-$  or  $-\text{N}=\text{N}-$ , may contain additional substituents such as ester, amide, carbamate, carbonate, sulfonate, ether, and the like, which may or may not serve as the connecting link between  $R$  and/or  $R'$  and the ultraviolet absorbing group.

When  $n$  is one,  $R$  and  $R'$  may be the same or different and when  $n$  is greater than one, the  $R$ 's may be the same or different and  $-\text{XX}-$  may be the same or different.

Specific radicals included within the generic descriptions given above for  $R$  and  $R'$  and the subgeneric descriptions for  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_4'$ , are the following:

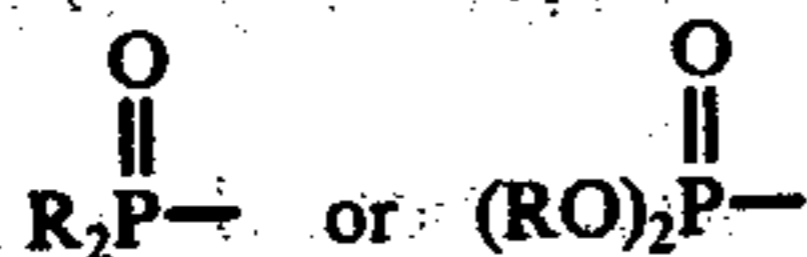
A. When  $-\text{X}-\text{X}-$  is  $-\text{O}-\text{O}-$  and  $n=1$ ,  $R$  and/or  $R'$  may be

1. hydrogen (but only one of said  $R$  or  $R'$  may be hydrogen)
2. acyl which may be acyclic, cyclic, bicyclic, unsaturated, or substituted, such as acetyl, propionyl, pelargonyl, lauroyl, stearoyl, cyclohexanecarbonyl, norbornane-5-carbonyl, perhydronaphthalene-2-carbonyl, crotonyl, 3-butenoyl, 3-chloropropionyl, 4-ethoxycarbonylbutyryl; cinnamoyl;
3. aroyl which may be substituted or unsubstituted and includes 5- and 6-membered heterocyclics such as benzoyl, toluoyl, naphthoyl, p-phenylbenzoyl, p-chlorobenzoyl, p-methoxybenzoyl, p-nitrobenzoyl, o-carboxybenzoyl, p-phenylazobenzoyl, nicotinoyl, 2-furoyl;
4. tert-alkyl and tert-cycloalkyl such as t-butyl, t-amyl, 1,1,3,3-tetramethylbutyl, 1-methylcyclohexyl, 1-methylcyclodecyl, 2-cyclohexylisopropyl;
5. tert-aralkyl such as tert-cumyl, p-isopropylcumyl, 2-(2-naphthyl)isopropyl, t-(p-chlorocumyl);
6. alkoxy-carbonyl such as methoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, 4-chlorobutoxycarbonyl, 2-ethylhexoxycarbonyl, tetradecyloxycarbonyl, hexadecyloxycarbonyl, octadecyloxycarbonyl, cyclohexyloxycarbonyl, cyclododecyloxycarbonyl, 1-perhydronaphthylloxycarbonyl;
7. carbamoyl, i.e.



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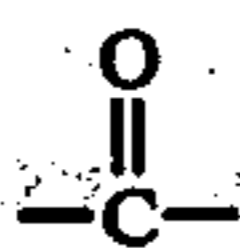
8. alkyl or dialkyl carbamoyl of 2-13 carbon atoms such as dimethylcarbamoyl, ethylcarbamoyl, N-ethyl-N-cyclohexylcarbamoyl;
9.  $\alpha$ -hydroxyalkyl such as  $\alpha$ -hydroxyethyl,  $\alpha$ -hydroxy- $\alpha$ -methylethyl,  $\alpha$ -hydroxy- $\alpha$ -methylpropyl,  $\alpha$ -hydroxy- $\alpha$ -ethyloctyl, 1-hydroxycyclohexyl, 1-hydroxycyclodecyl;
10.  $\alpha$ -hydroperoxyalkyl such as  $\alpha$ -hydroperoxyethyl,  $\alpha$ -hydroperoxy- $\alpha$ -methylethyl,  $\alpha$ -hydroperoxy- $\alpha$ -methylpropyl,  $\alpha$ -hydroperoxy- $\alpha$ -ethyloctyl, 1-hydroperoxycyclohexyl, 1-hydroperoxycyclodecyl;
11. alkyl- and cycloalkylsulfonyl such as t-butylsulfonyl, t-amylsulfonyl, heptylsulfonyl, eicosylsulfonyl, cyclopentylsulfonyl, cyclohexylsulfonyl, methylcyclohexylsulfonyl, perhydronaphthylsulfonyl, 4-cyclohexylcyclohexylsulfonyl;
12. tert-alkoxyalkyl such as 2-methoxyisopropyl, 1-methoxy-1-methyloctadecyl, 1-methoxycyclohexyl, 1-ethoxycyclododecyl;
13. organomineral having the formula  $(Q)_3M-$  or  $(Q)_2M'-$  where M=silicon, germanium or tin, M' is boron, and Q=alkyl of 1-11 carbon atoms, phenyl, or benzyl such as trimethylsilyl, triphenylsilyl, triethylsilyl, tripropylgermanium, triphenylgermanium, trimethyltin, tricyclohexyltin, triphenyltin, dioctylboron, didecylboron, dicyclodecylboron, dibenzylboron; organophosphorus having the formula



where R = alkyl of 1-8 carbon atoms or phenyl such as diethylphosphate, dimethylphosphate, diphenylphosphinic, di-n-octylphosphate, dibutylphosphinic.

B. When  $-X-X-$  is  $-O-O-$  and  $n=2$ , R can be any of the above radicals under group A and R' can be

1. alkylidene or cycloalkylidene such as ethylidene,



2. alkylidene or cycloalkylidene such as ethylidene, isopropylidene, pentylidene, 1-methylethylidene, 1-heptylpentylidene, 1-nonylheptylidene, cyclohexylidene, cyclododecylidene, cyclopropylidene;

3. organomineral having the formula  $(Q)_2M=$  or  $QM'=$  where Q, M, and M' are as defined above in A 13), such as dimethylsilyl, diphenylsilyl, diethylsilyl, dipropylgermanium, diphenylgermanium, dimethyltin, dicyclohexyltin, diphenyltin, octylboron, undecylboron, cyclodecylboron, benzylboron;

4. di-tert-alkylene or cycloalkylene such as tetramethylethylene, 1,1,4,4-tetramethyltetramethylene, 1,1,8,8-tetraethyloctamethylene,  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,4-cyclohexenylenedimethylene;

5. di-tert-aralkylene such as  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-p-phenylenedimethylene,  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-p,p'

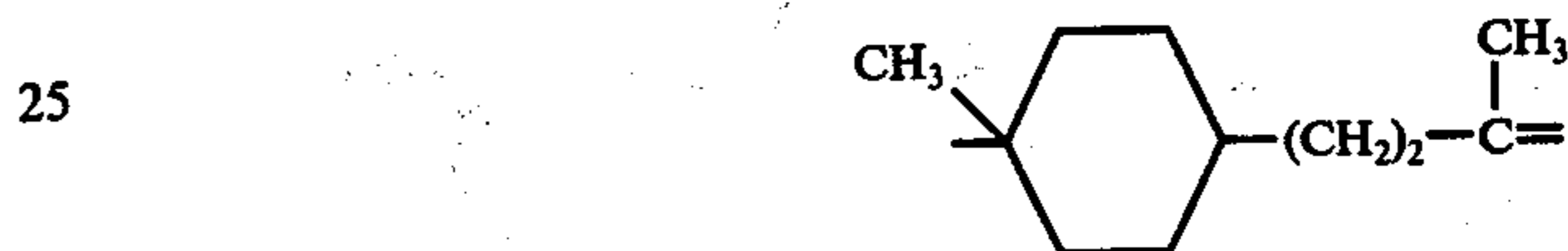
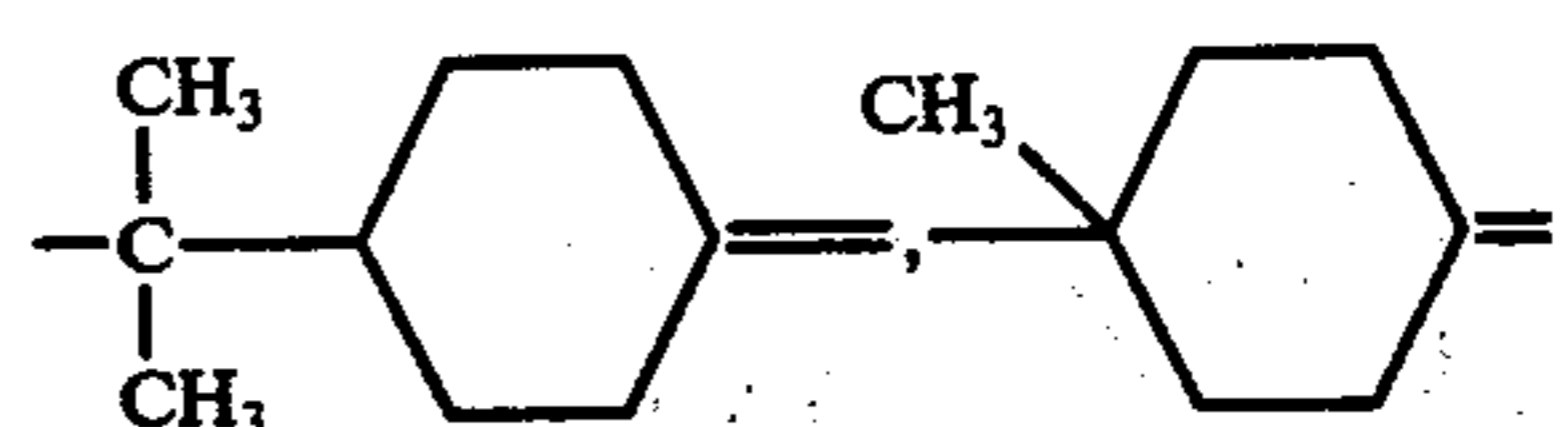
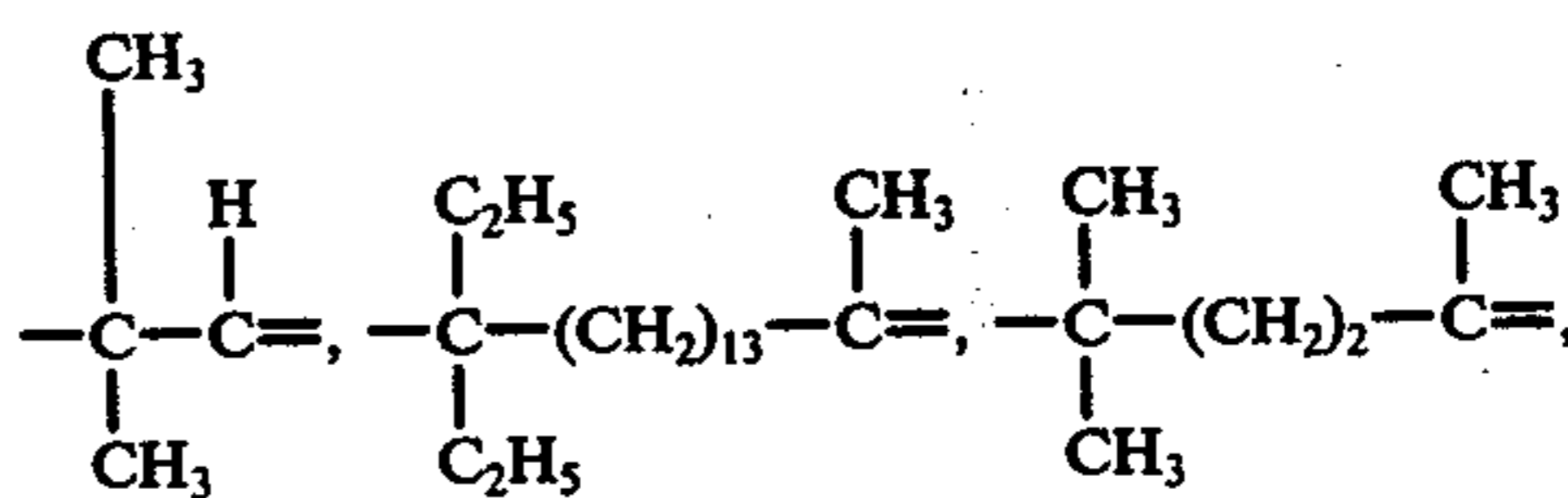
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biphenylenedimethylene,  $\alpha,\alpha,\alpha',\alpha'$ -tetraethyl-1,4-naphthylenedimethylene;

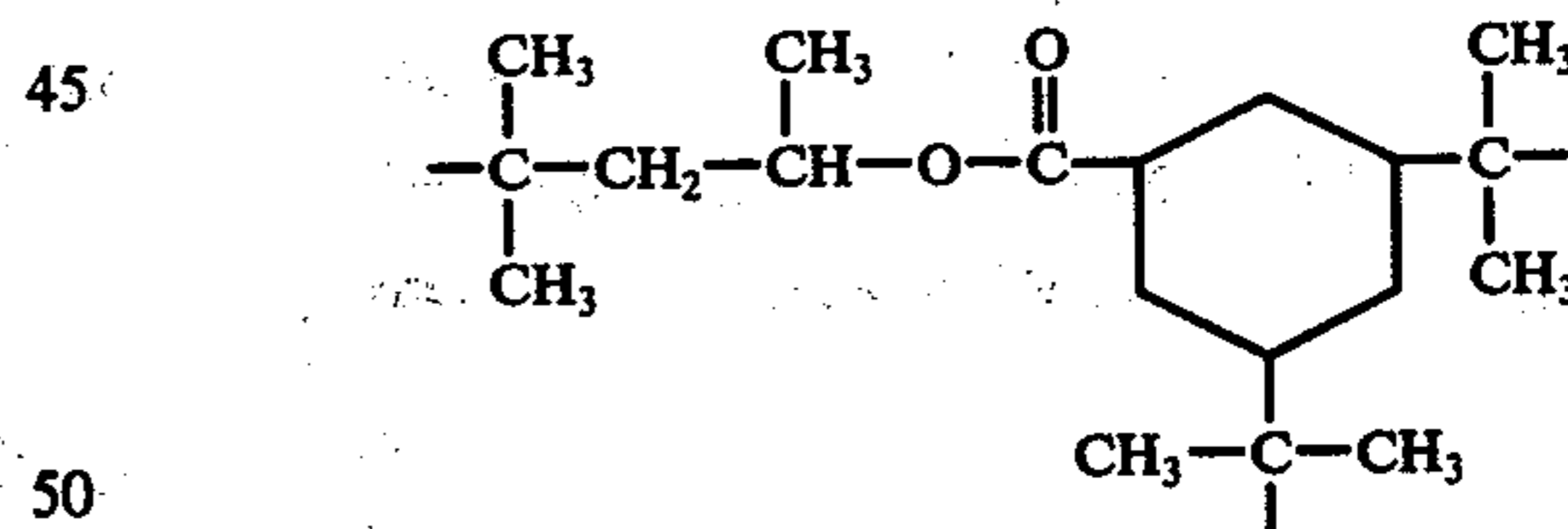
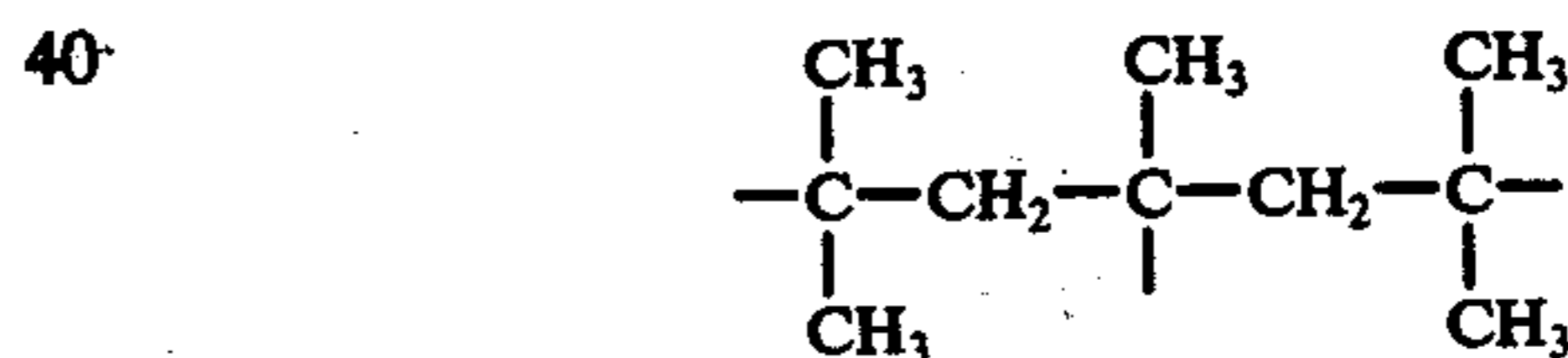
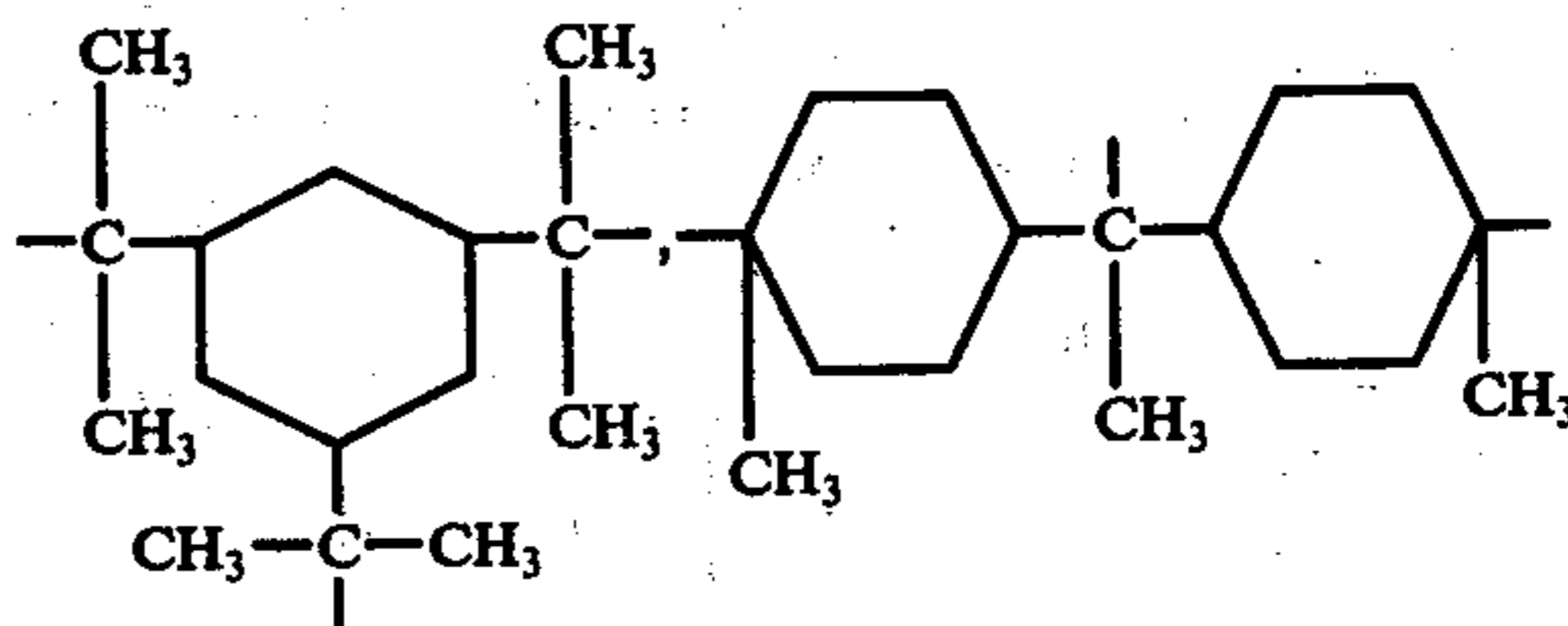
C. When  $-X-X-$  is  $-O-O-$  and  $n=3$ , R can be any of the above radicals under group A and R' can be

1. tert-aralkyl-di-tert-aralkylene such as  $\alpha,\alpha,\alpha',\alpha',\alpha'',\alpha''$ -hexamethyl-s-phenyltrimethylene,  $\alpha,\alpha,\alpha',\alpha',\alpha'',\alpha''$ -hexaethyl-s-phenyltrimethylene;

2. tert-alkylalkylidene, cycloalkylalkylidene, cycloalkylcycloalkylidene or alkylcycloalkylidene such as

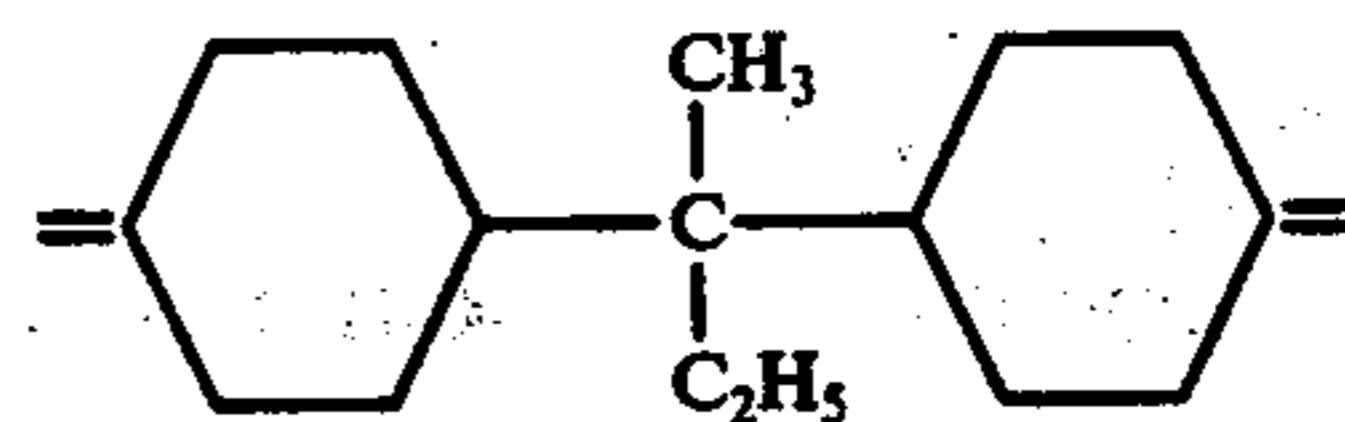


3. tert-alkyl-di-tert-alkylene such as



4. organomineral having the formula  $QM \equiv$  where Q and M are as defined above in A 13) such as methylsilyl, phenylsilyl, ethylsilyl, propylgermanium, phenylgermanium, methyltin, cyclohexyltin, phenyltin.

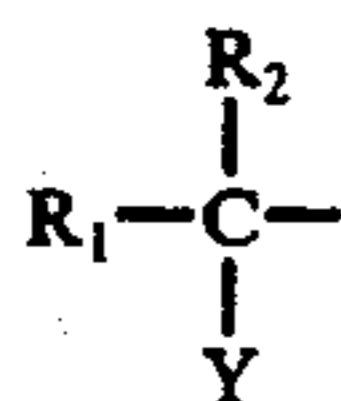
D. When  $-X-X-$  is  $-O-O-$  and  $n=4$ , R can be any of the above radicals under group A and R' can be 1) dialkylidene such as



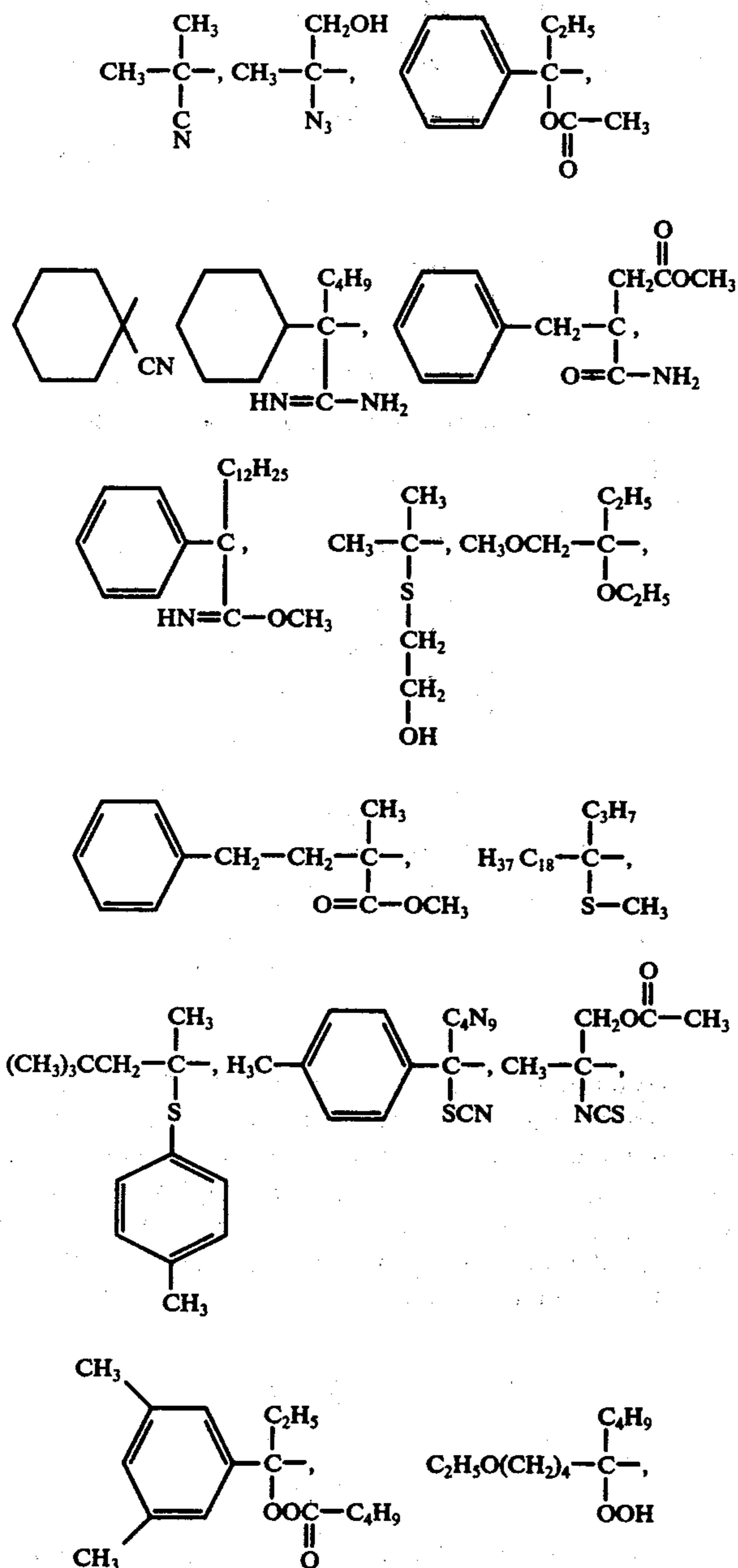
E. When  $-X-X-$  is  $-N=N-$  and  $n=1$ , R and R' may be

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1. alkyl such as methyl, ethyl, isopropyl, t-butyl, t-amyl, t-octyl, eicosyl, 1,1-dimethyldodecyl;
2. cycloalkyl such as cyclopropyl, cyclobutyl, 1-methylcyclopentyl, cyclohexyl, cyclooctyl, cyclodecyl;
3. aralkyl such as benzyl, phenethyl, t-cumyl, p-isopropyl-t-cumyl, p-phenyl-t-cumyl, 2-(2-naphthyl)-isopropyl;
- 4.

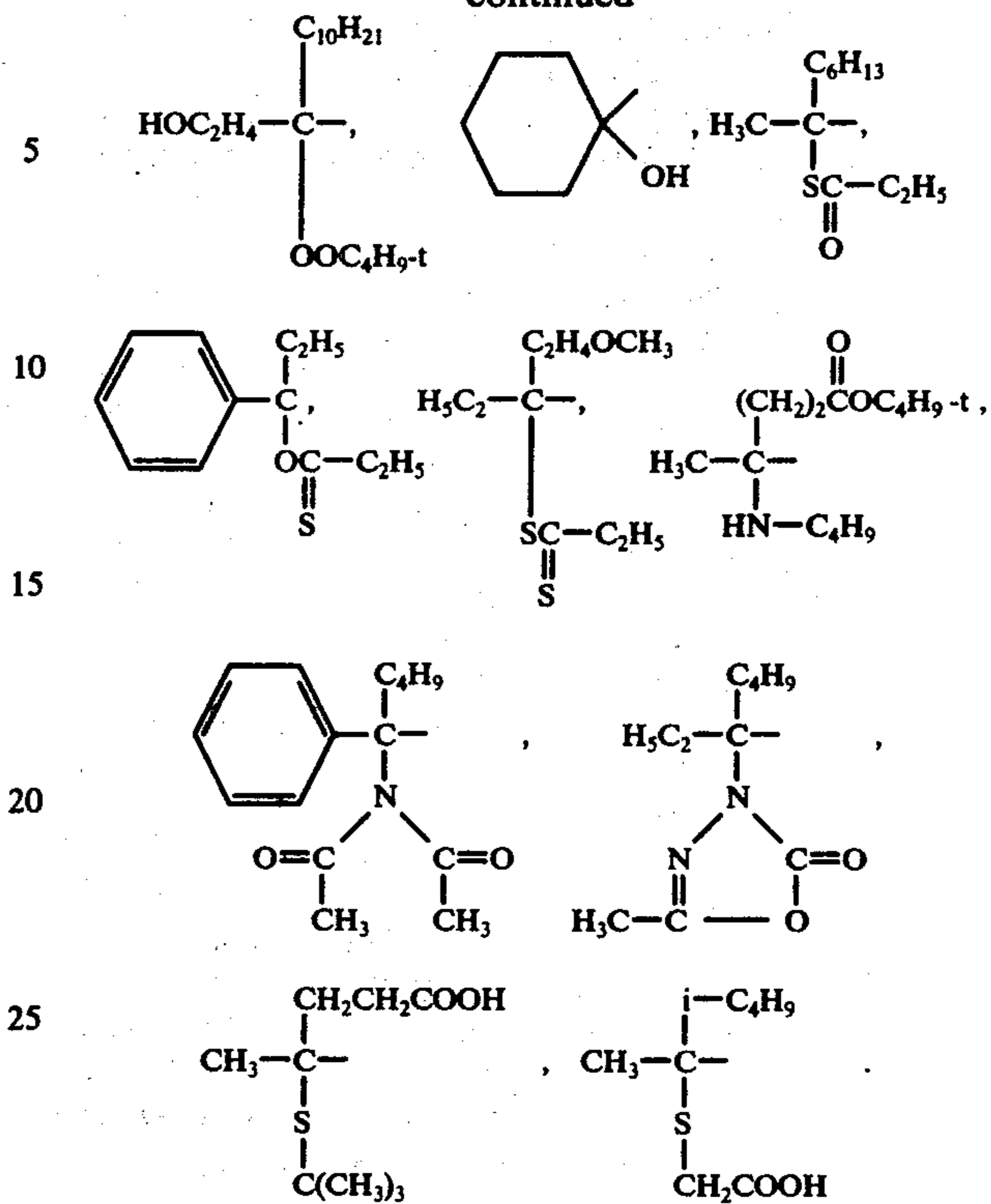


which includes such radicals as



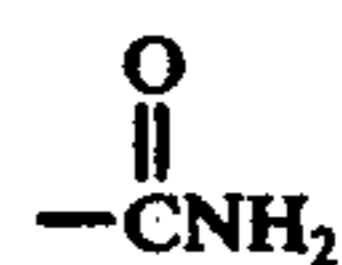
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F. When  $-X-X-$  is  $-N=N-$  and  $n=1$ , one but not both of R and R' may be, in addition to those in E) above

1. aryl such as phenyl, tolyl, xylyl, naphthyl, p-phenylphenyl;
2. acyl such as those radicals listed above in A 2).
3. aroyl, such as those radicals listed above in A 3);
4. carbamoyl,



5. alkyl carbamoyl such as those radicals listed above in A 8);

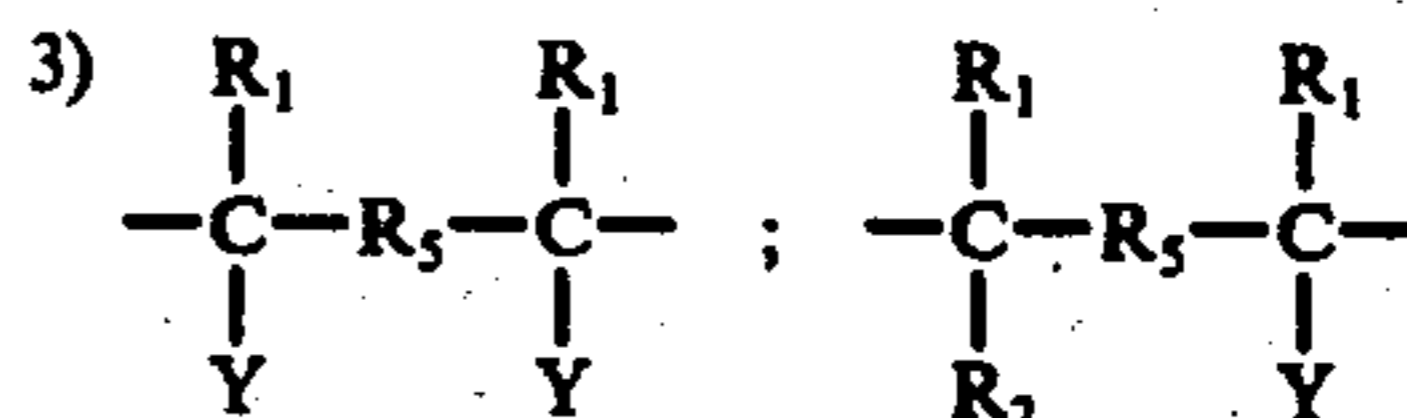
6.  $-\text{CO}_2\text{Na}$  and  $-\text{CO}_2\text{K}$

7. alkoxy-carbonyl and aryloxycarbonyl such as those radicals listed above in A 6) and phenyloxycarbonyl, tolyloxycarbonyl, xylyloxycarbonyl;

G. When  $-X-X-$  is  $-N=N-$ ,  $n=1$ , and R is a carbamoyl group, R' can also be an alkoxy-carbonyl or an aryloxycarbonyl as exemplified above in F 7).

H. When  $-X-X-$  is  $-N=N-$  and  $n=2$ , R can be any of the radicals above under E, F and G, and R' is

1. di-tert-alkylene and cycloalkylene such as those exemplified above in B 4);
2. di-tert-aralkylene such as those exemplified above in B 5);
- 3.



where  $R_1$ ,  $R_2$  and Y are as defined above and  $R_5$  is alkylene or cycloalkylene such as methylene, ethylene, hexylene, decylene, cyclohexylene, oxydiethylene;

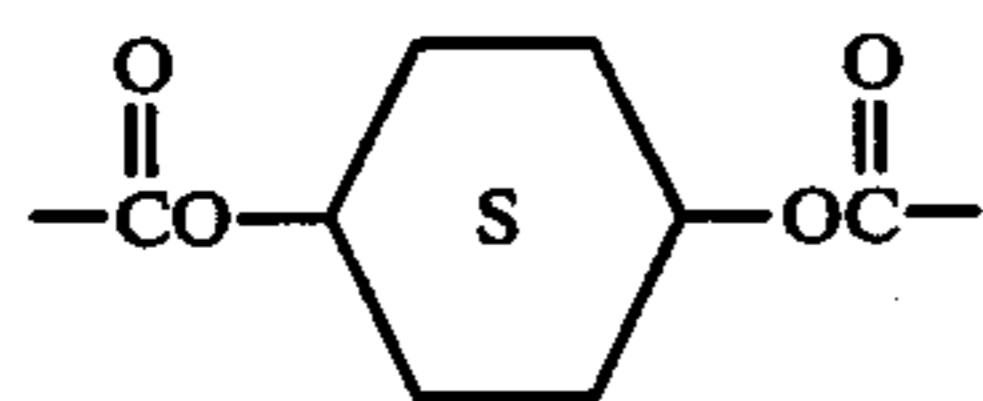
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J. When  $-X-X-$  is  $-N=N-$  and  $n=2$ , R can be any definition under E above and R' can be, in addition to those mentioned in H

1. diacyl such as malonoyl, succinoyl, glutaroyl, sebacoyl;
2. diaroyl such as terephthaloyl, isophthaloyl, 4,4'-biphenylenedicarbonyl;
3. arylyne such as p-phenylene, 4,4'-biphenylene, 1,4-naphthylene;
- 4.

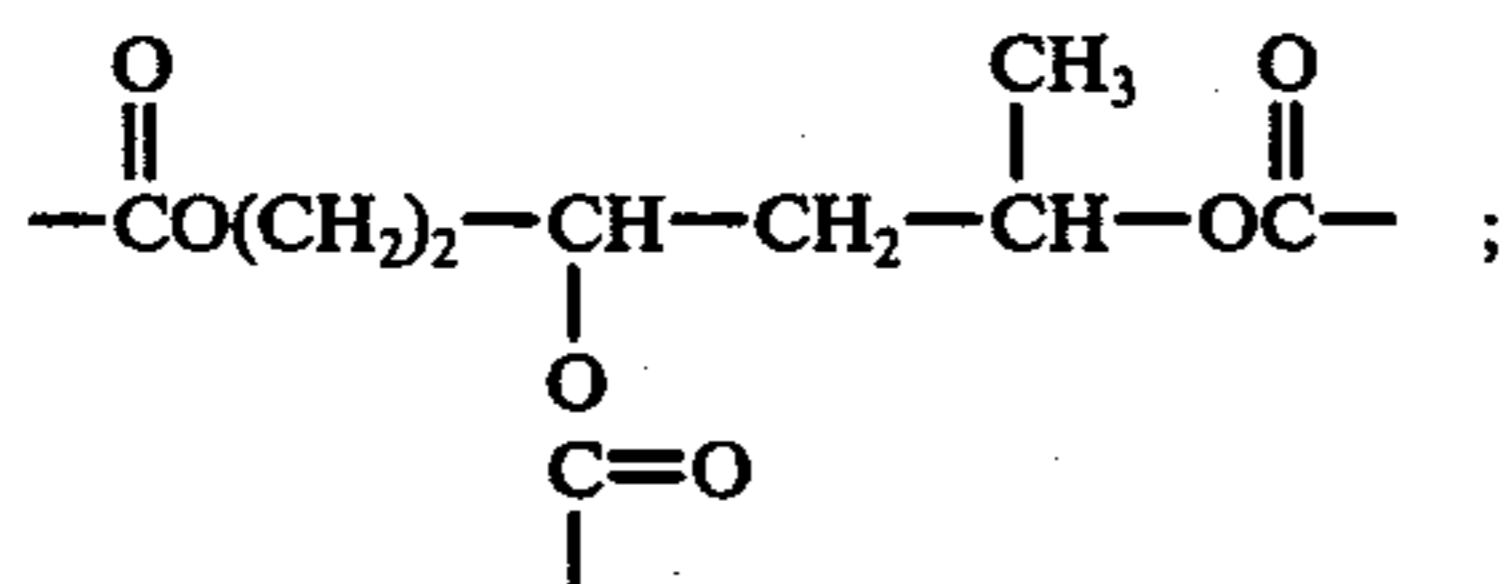


such as

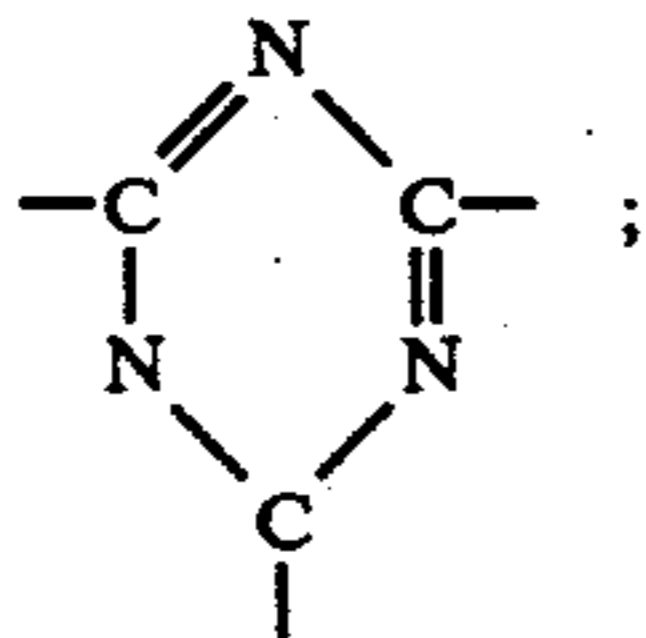


K. When  $-X-X-$  is  $-N=N-$  and  $n=3$  R can be any radical defined under E above and R' can be:

1. tert.-alkyl-di-tert.-arylylene such as those exemplified in C1;
2. tert.-alkyl-di-tert.-alkylene such as those exemplified in C3;
3. trialkoxycarbonyl such as

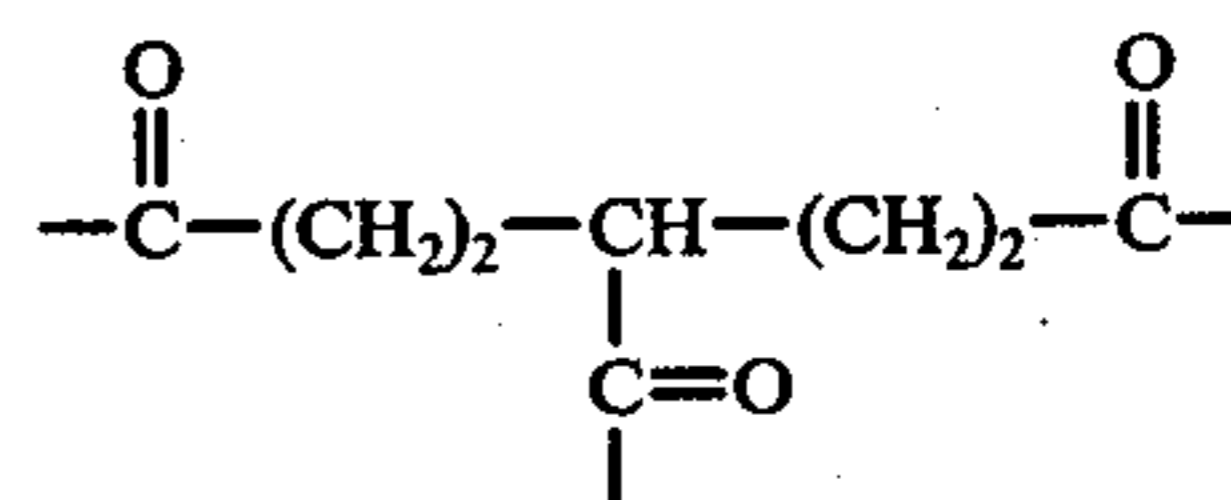


4. triazinyl

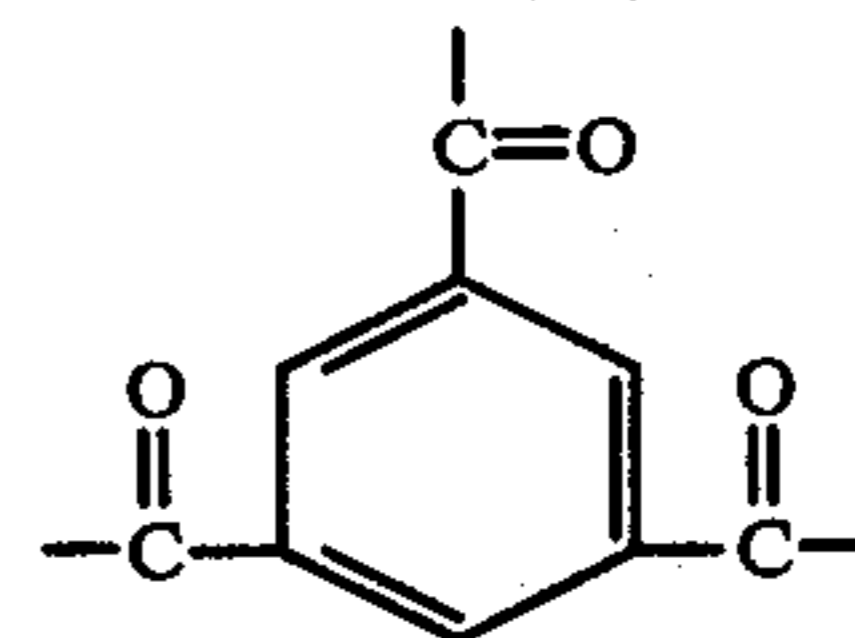


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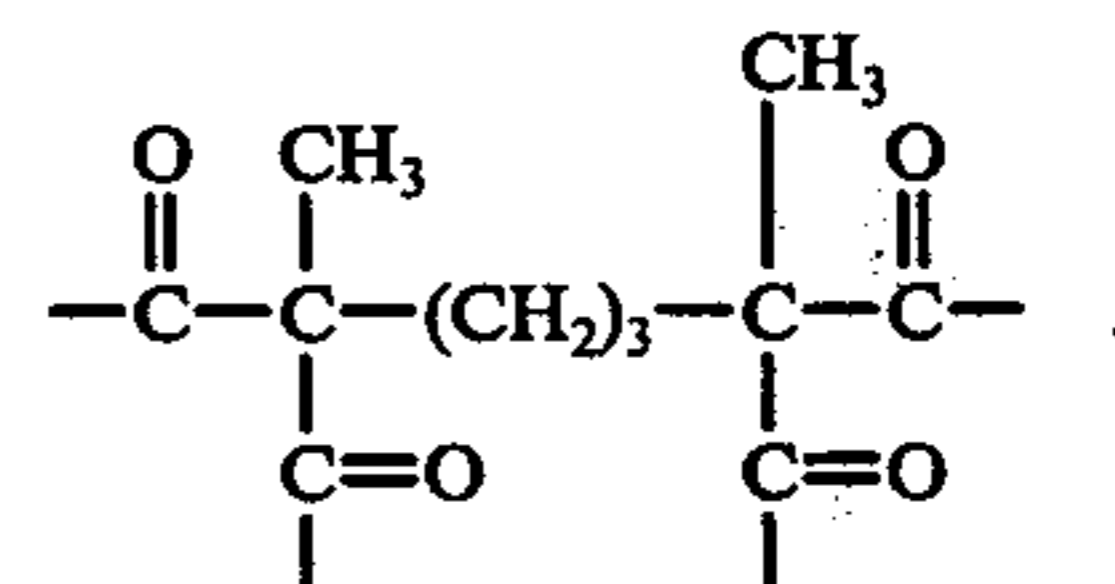
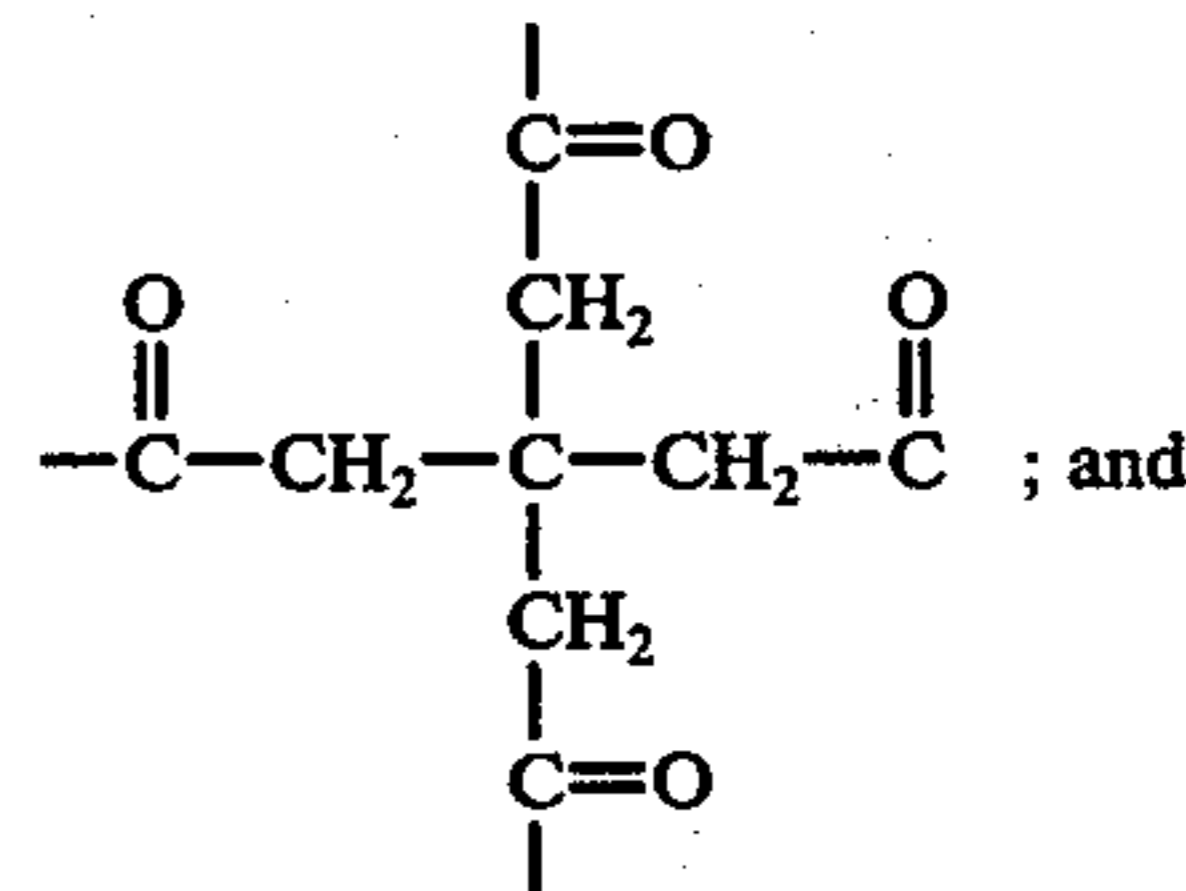
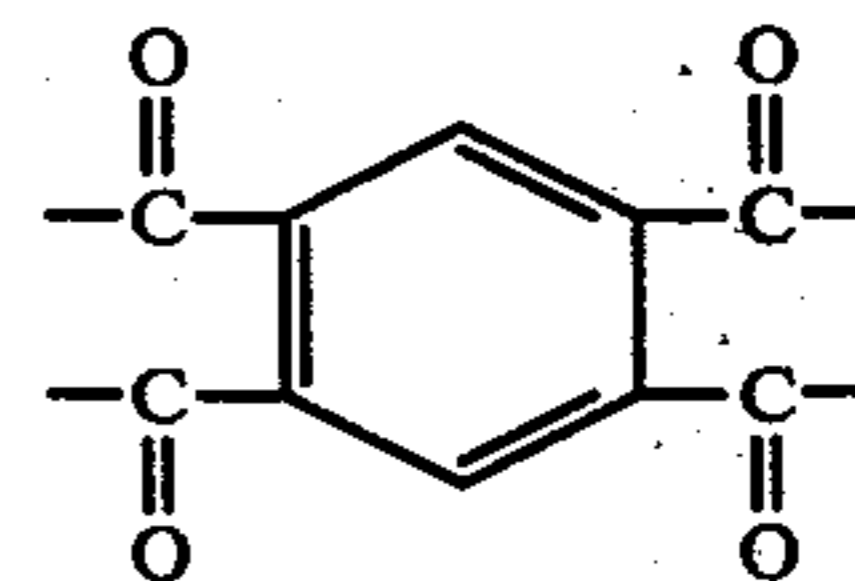
5. triacyl and triaroyl, such as



and

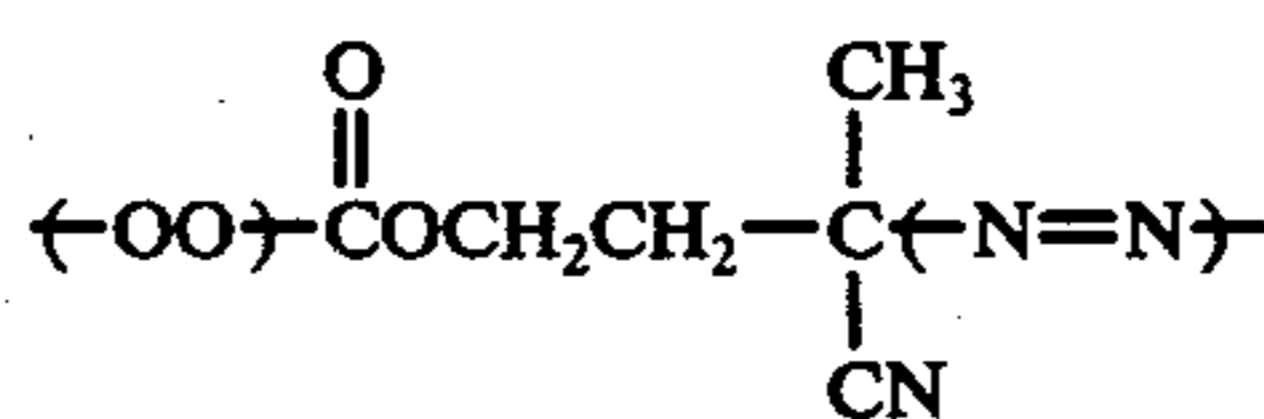


L. When  $-X-X-$  is  $-N=N-$  and  $n=4$  R can be any radical defined under E above and R' can be tetraacyl and tetraaroyl, such as

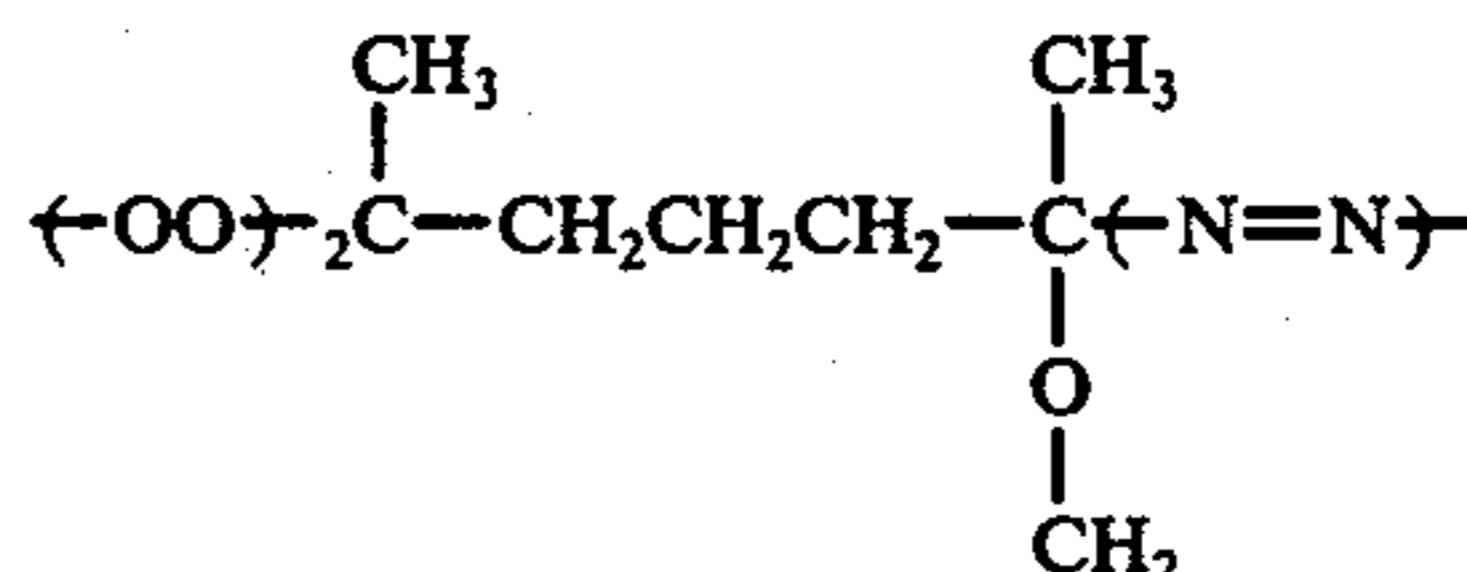


M. When  $n$  is 2-4 and at least one of the  $-XX-$  groups is  $-O-O-$  and at least one of the  $-XX$  groups is  $-N=N-$ , the R connected to  $-OO-$  can be any radical listed under A above and the R connected to  $-N=N-$  can be any radical listed under E above the R<sup>1</sup> is a di-, tri-, or tetravalent radical composed of a combination of those radicals listed under A, B, and C for the  $-OO-$  linkage and those radicals listed under E, H, and K for the  $-N=N-$  linkage to R<sup>1</sup>.

Some examples of such R<sup>1</sup> combinations are:

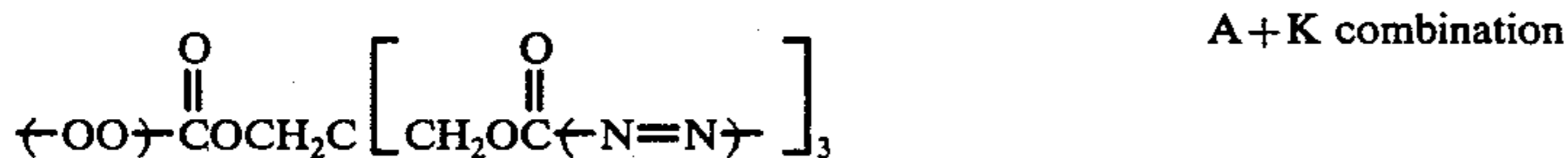
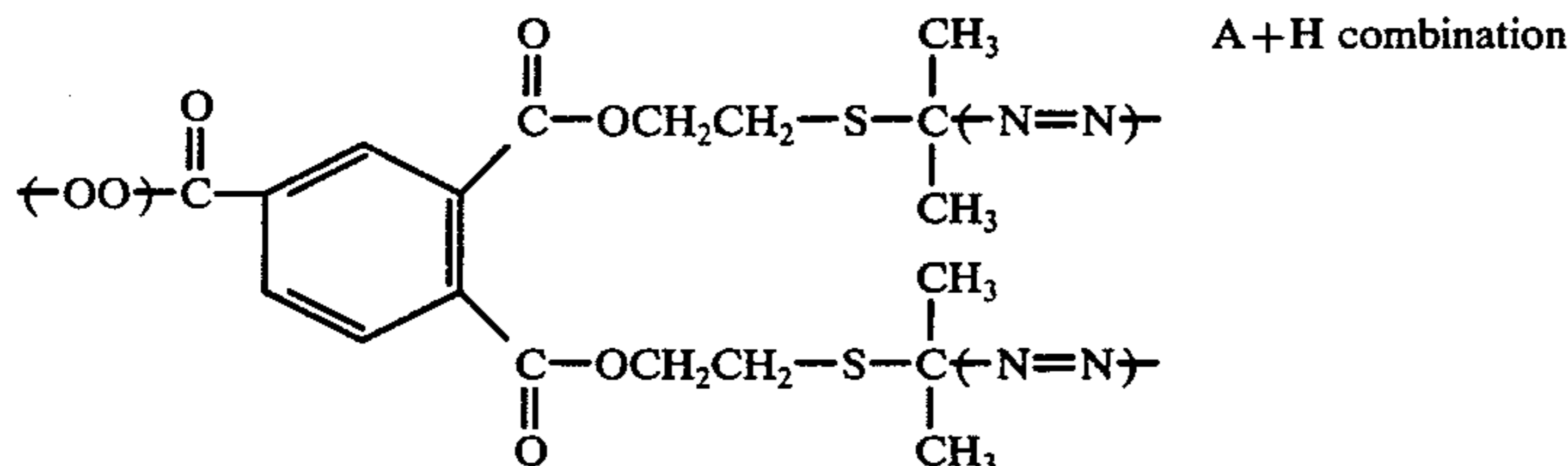
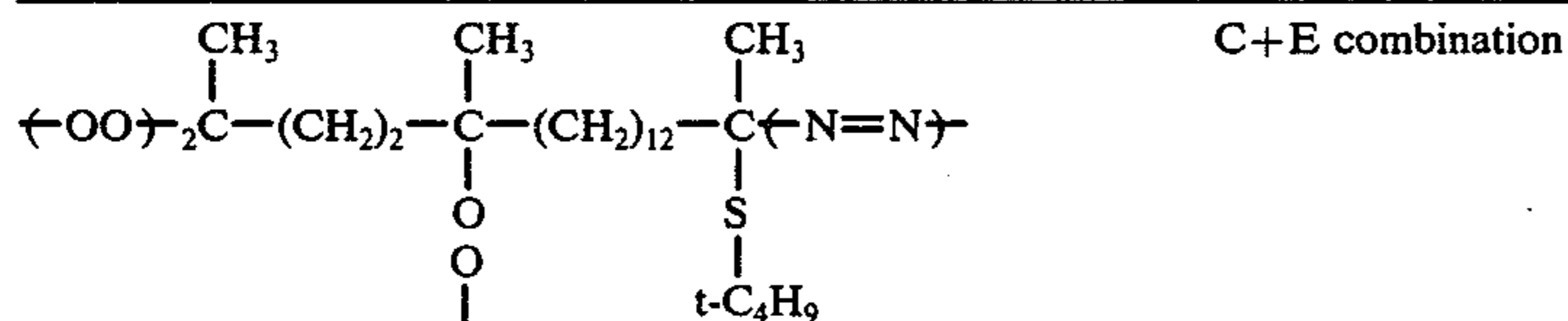


A+E combination



B+E combination

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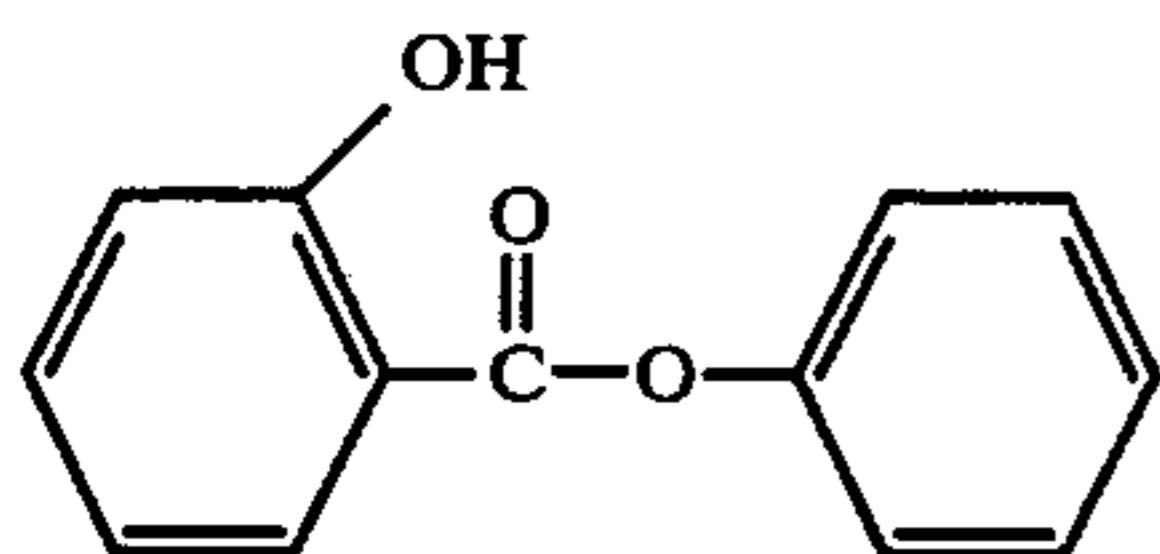
Compounds having aliphatic azo groups and peroxide groups in the same molecule and their preparation are disclosed in co-pending application Ser. No. 37,310 entitled "Compounds having peroxy and aliphatic azo groups and methods using these as initiators".

In the foregoing descriptions,  $R_1$  and  $R_2$  are substituted or unsubstituted and are when not joined together alkyl of 1-20 carbon atoms or cycloalkyl of 3-6 carbon atoms.  $R_1$  and  $R_2$  when joined together form an alkylene of 2-30 carbon atoms. Typical examples of alkyl are methyl, ethyl, propyl, butyl, hexyl, decyl, dodecyl, octadecyl, and eicosyl. Typical examples of cycloalkyl are cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. Typical examples of alkylene are ethylene, trimethylene, hexamethylene, octadecamethylene, tricosamethylene and triacontamethylene.  $R_3$  is a tert.-alkyl of 4-8 carbon atoms, a tert.-cycloalkyl of 4-8 carbon atoms or a tert.-aralkyl of 9-15 carbon atoms. Typical examples of such are t-butyl, t-amyl, t-hexyl, t-heptyl, t-octyl, 1,1,3,3-tetramethylbutyl, 1-methylcyclohexyl, 2-cyclobutylisopropyl, t-cumyl, p-isopropylcumyl, 2-(2-naphthyl)isopropyl, t-(p-chlorocumyl).

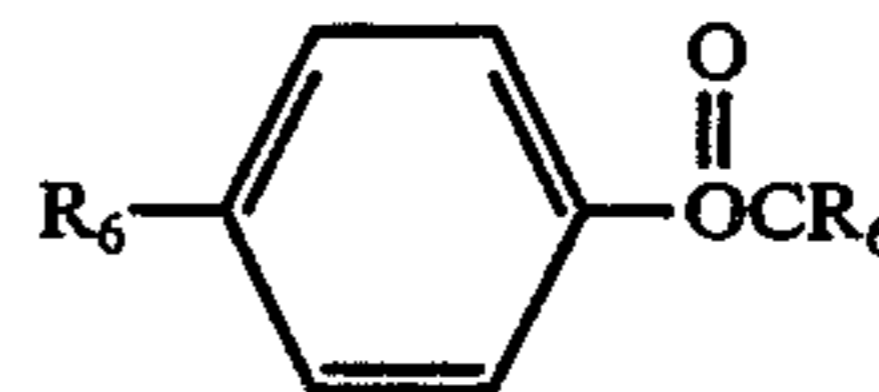
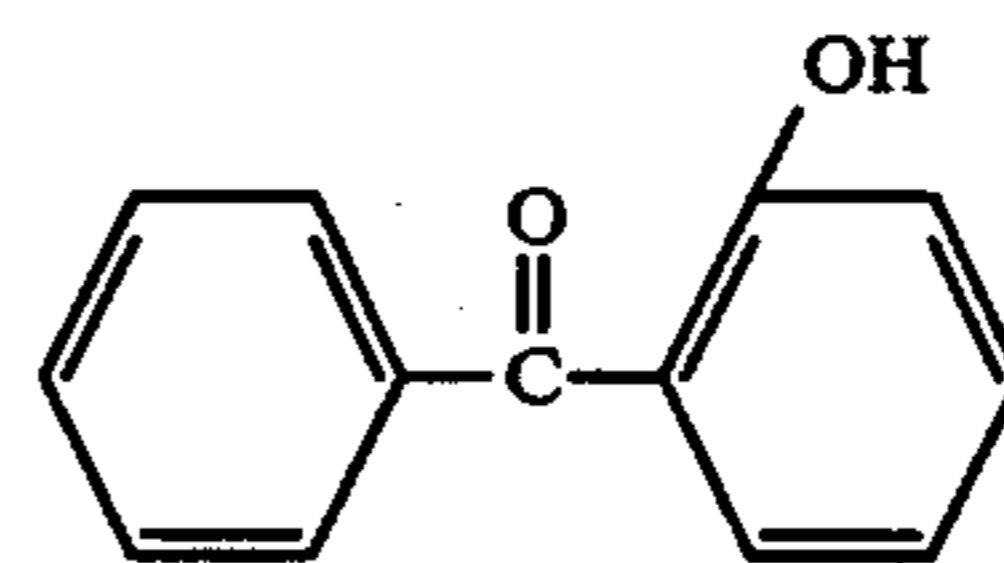
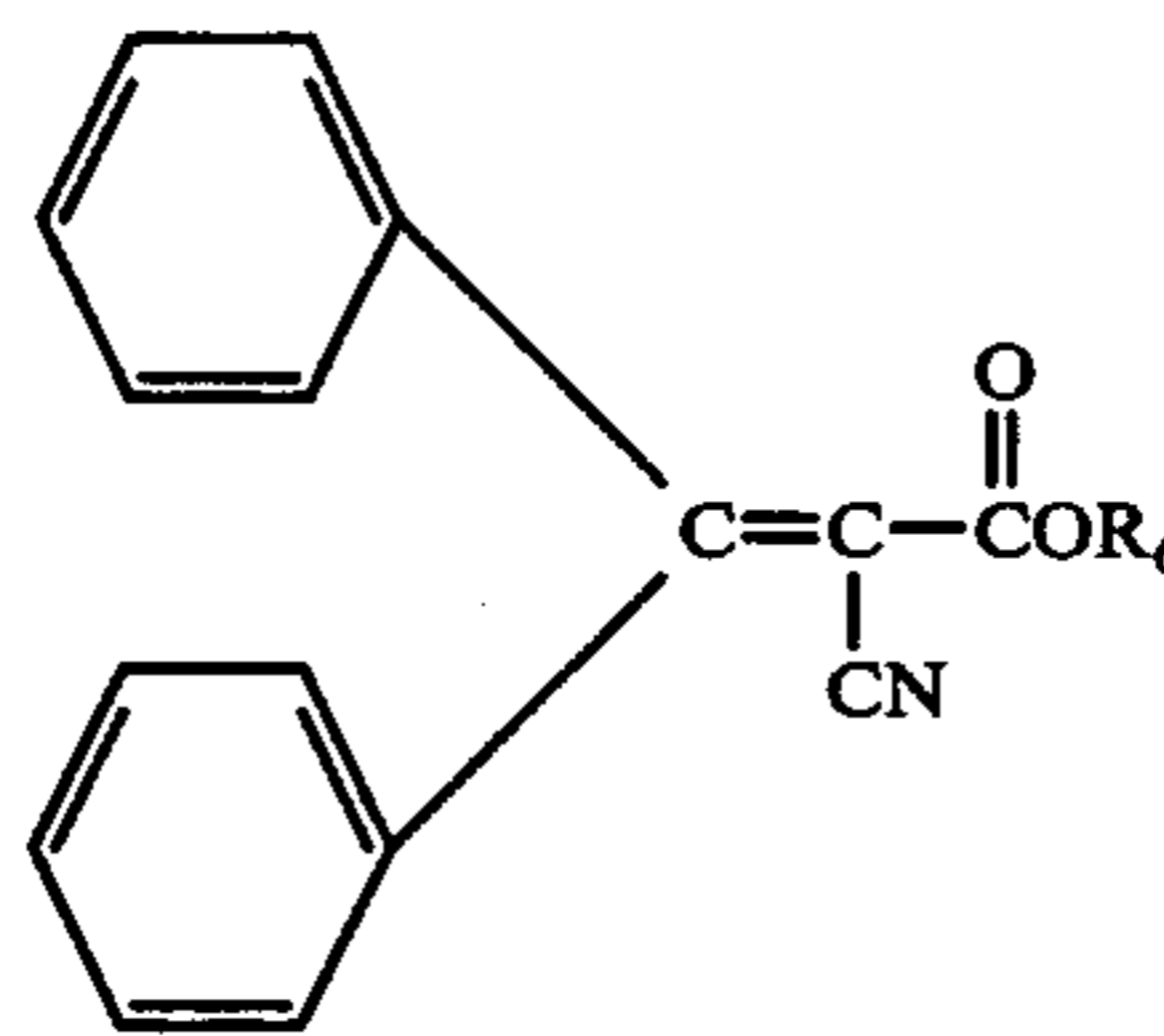
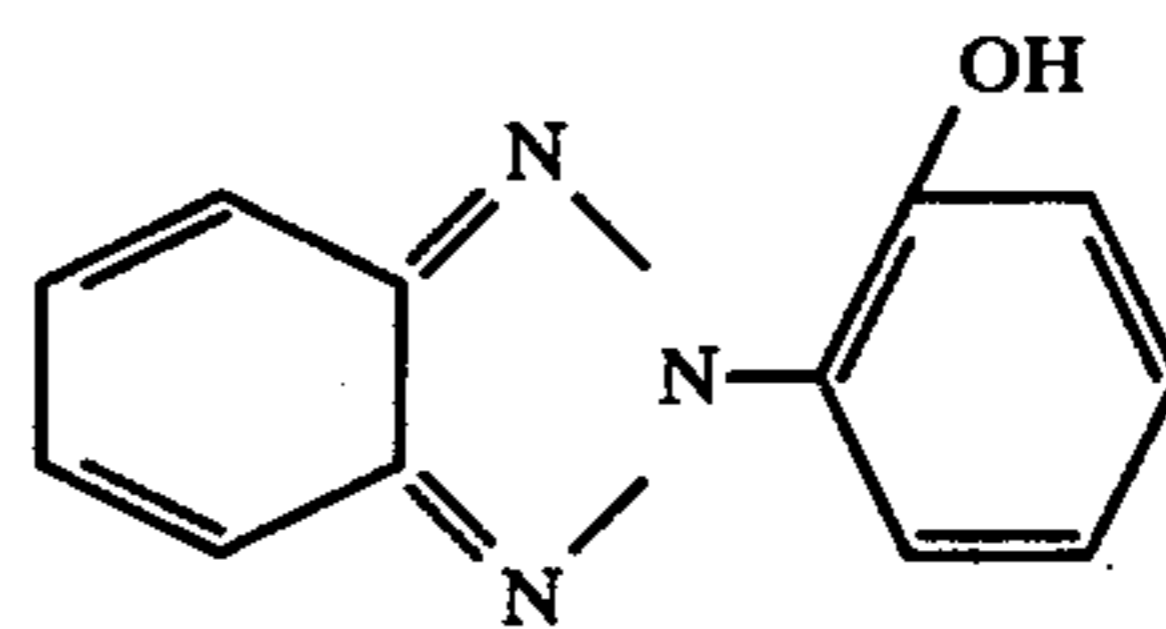
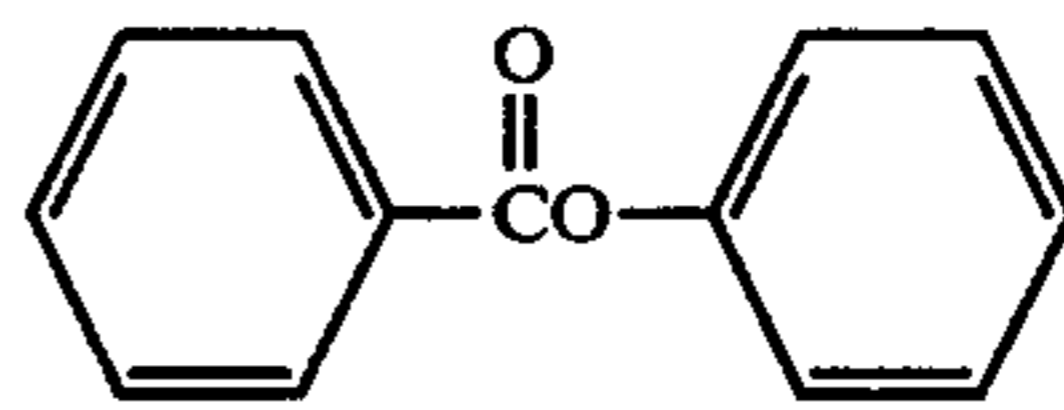
$R_4$  and  $R_4'$  are alkyl of 1-6 carbon atoms such as methyl, ethyl, propyl, hexyl; cycloalkyl of 3-6 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl; aryl of 6-12 carbon atoms such as phenyl, biphenyl, naphthyl, tolyl, xylyl; alkylene of 1-6 carbon atoms, such as ethylene, trimethylene, tetramethylene, hexamethylene; and arylene of 6-12 carbon atoms, such as phenylene, biphenylene, naphthylene.

$R_5$  is alkylene of 1-10 carbon atoms, such as methylene, ethylene, tetramethylene, hexamethylene, decamethylene, or cycloalkylene of 3-10 carbon atoms, such as cyclopropylene, cyclobutylene, cyclohexylene, cyclodecylene, 1,4-dimethylenecyclohexane.

Ultraviolet light stabilizing compounds are well known, principally among those are phenyl salicylates, the orthohydroxy-benzophenones, the cyano-acrylates, and benzotriazoles. Particularly useful among these are the following compounds:



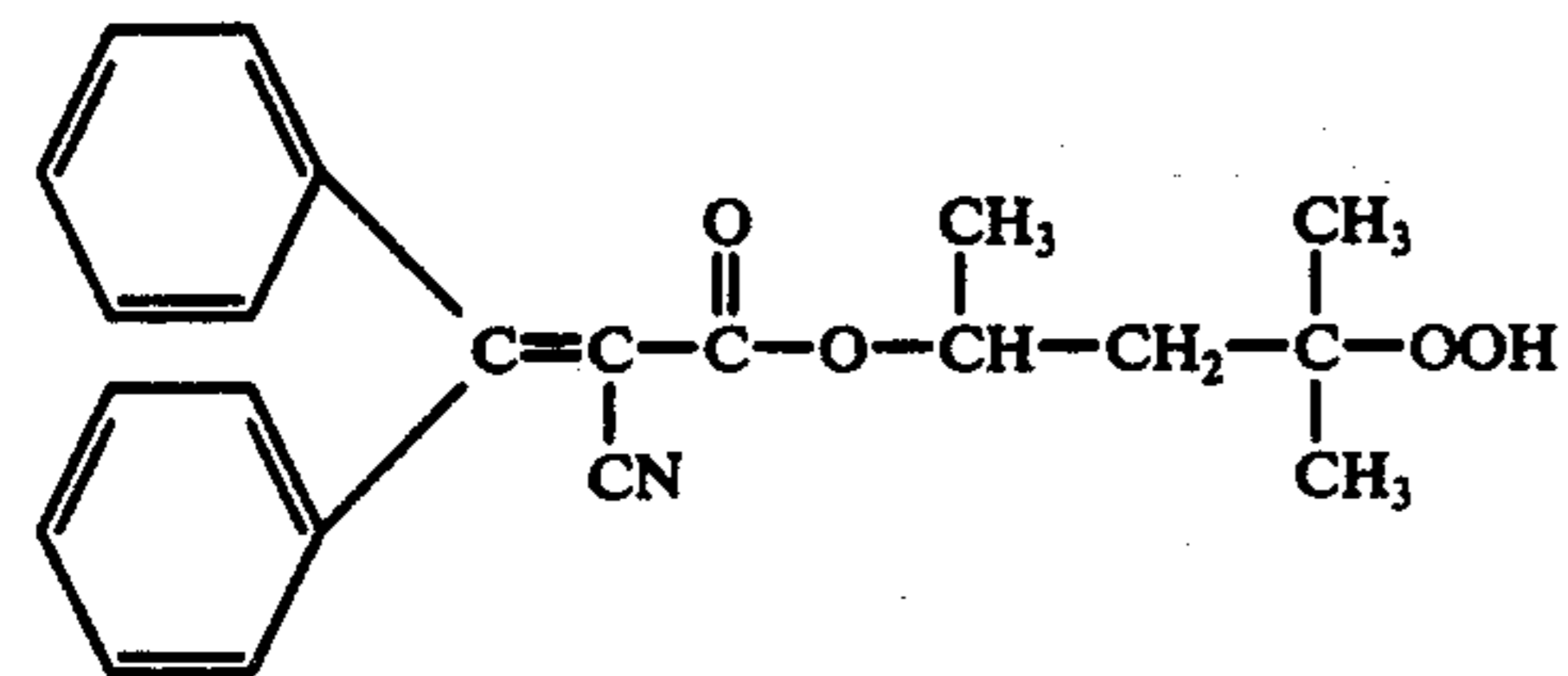
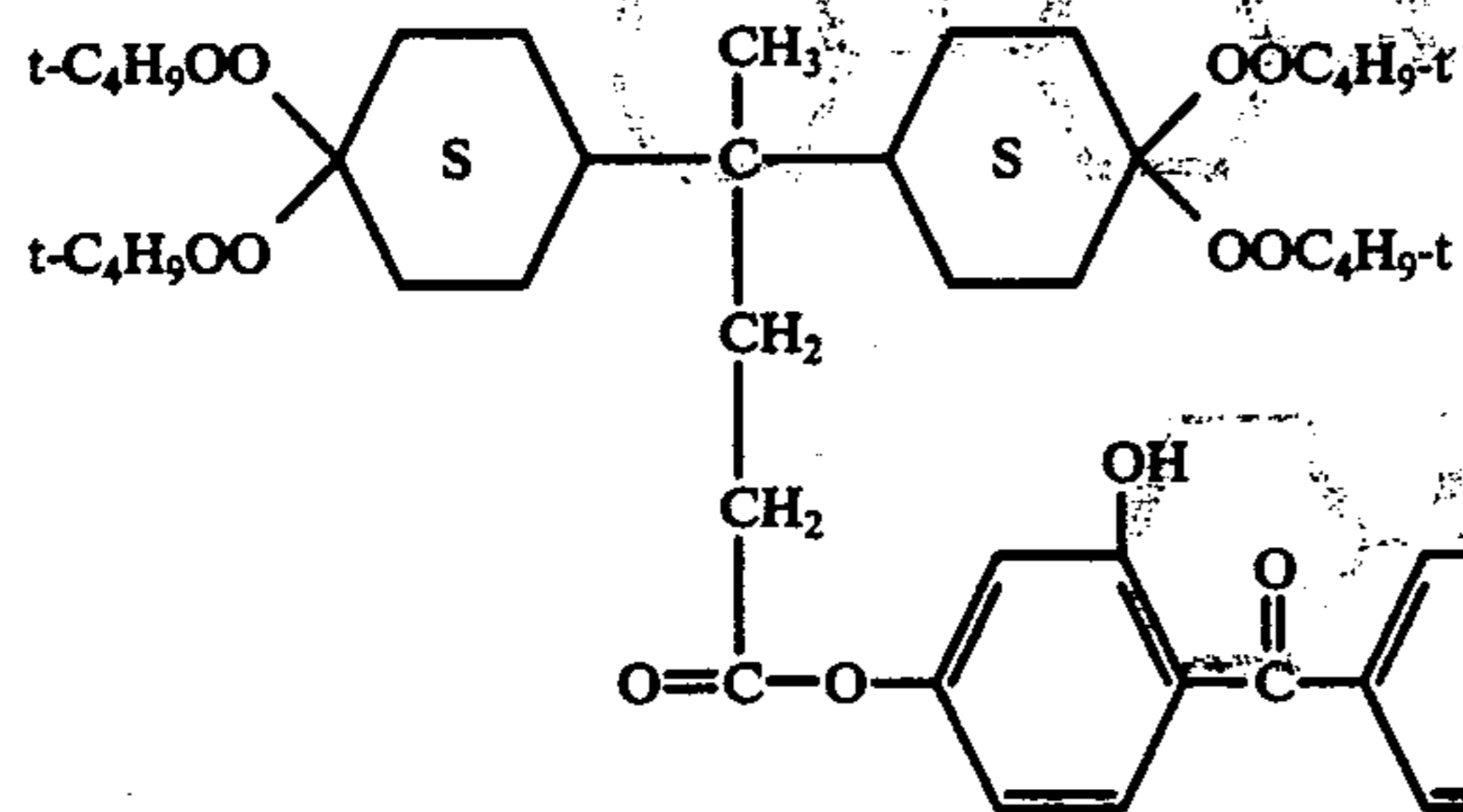
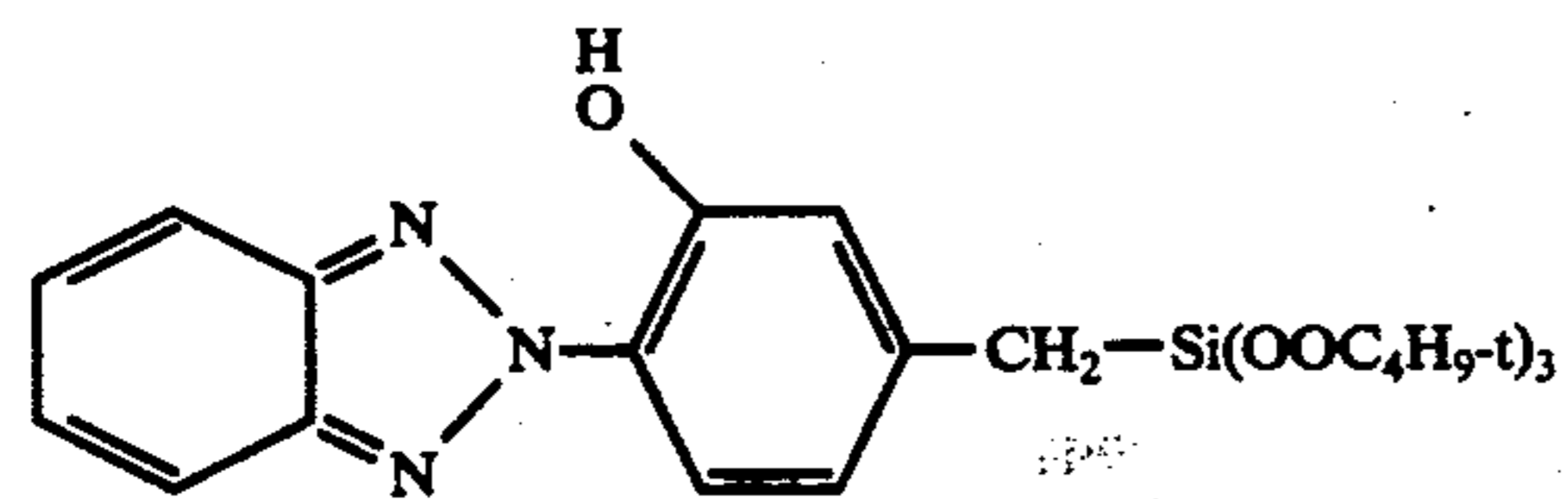
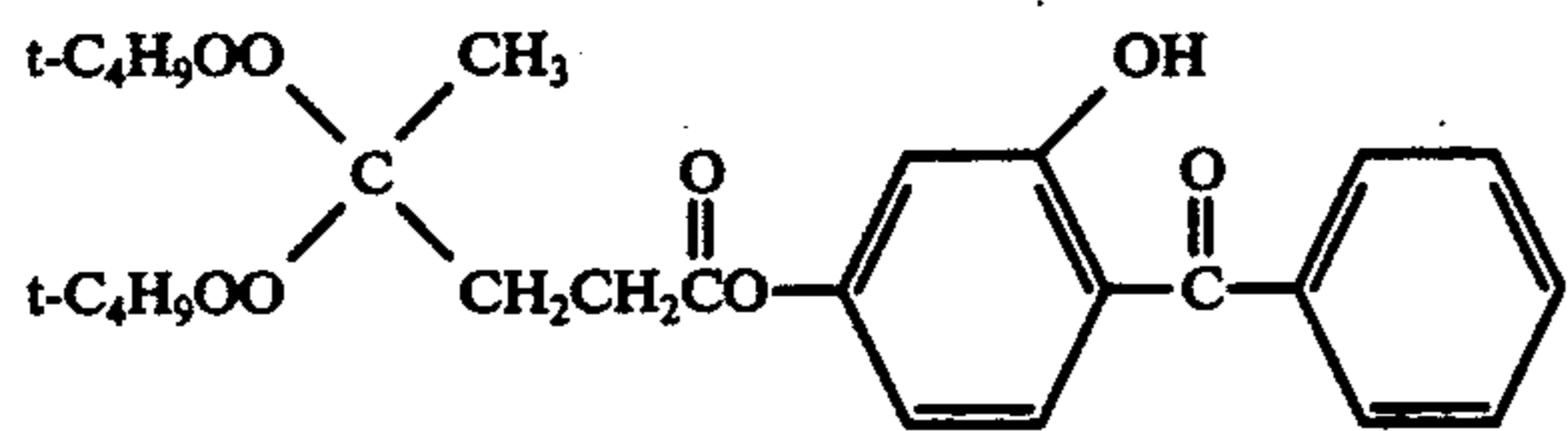
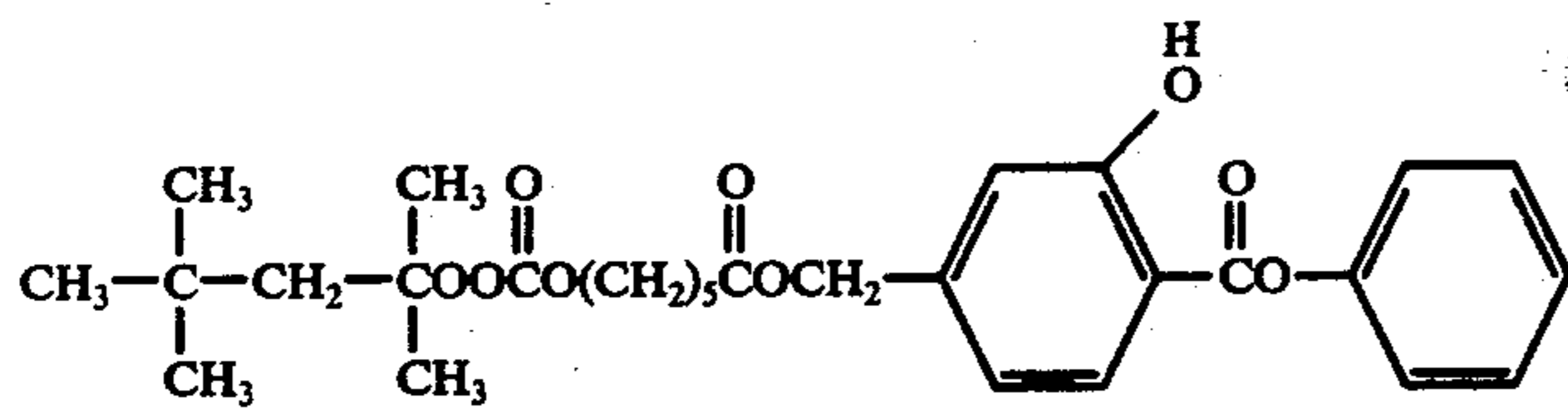
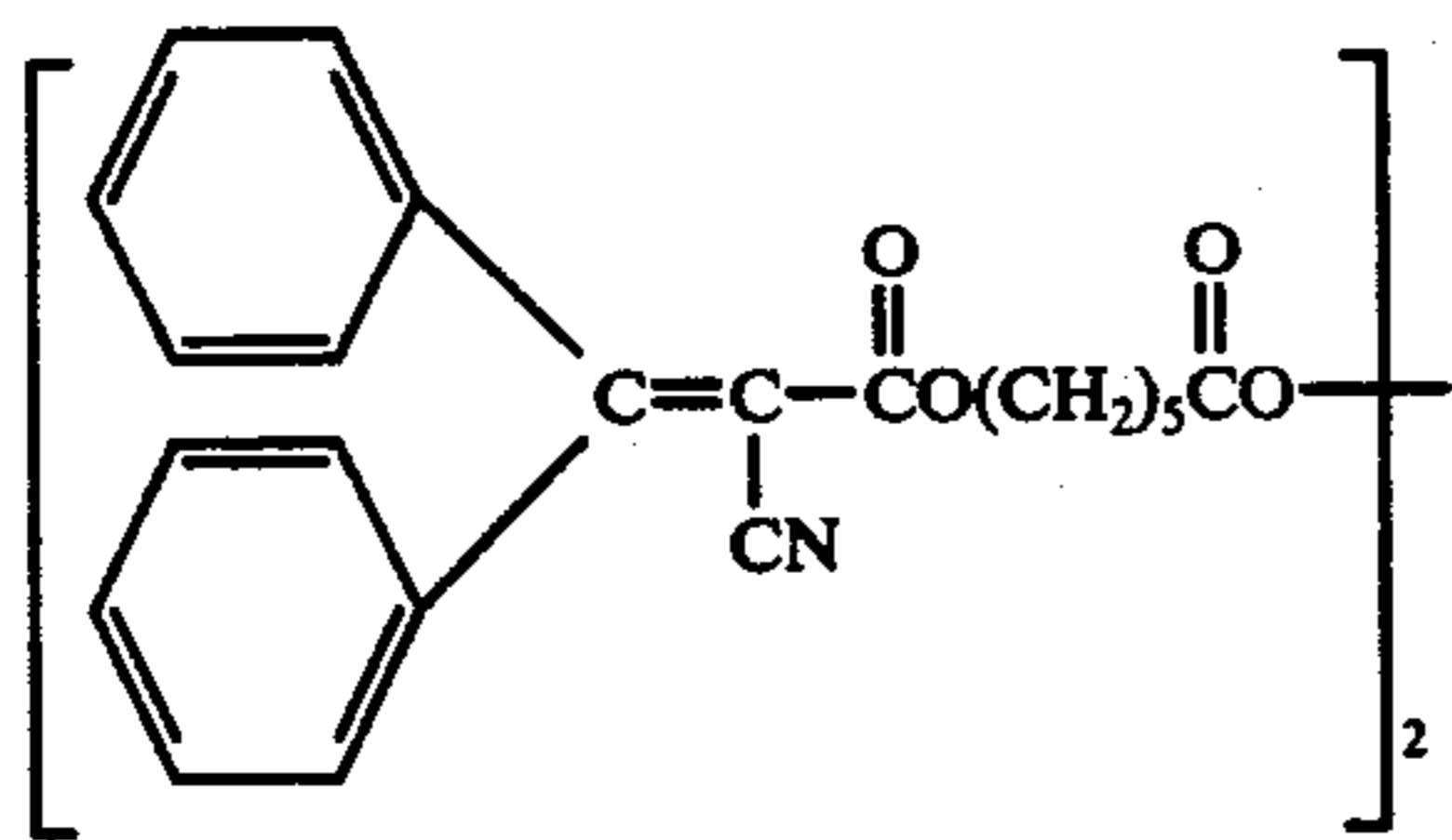
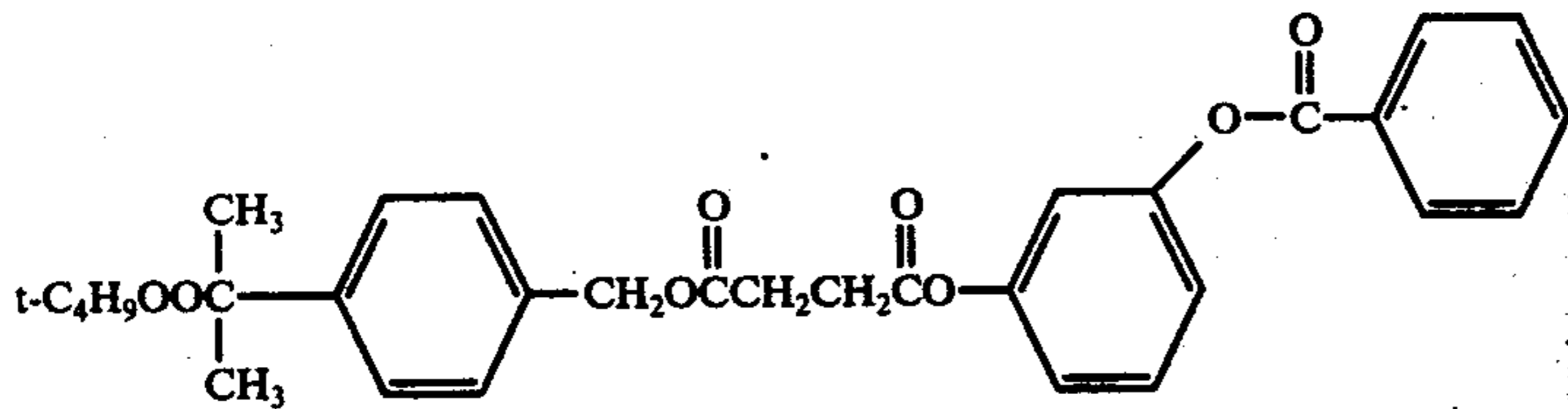
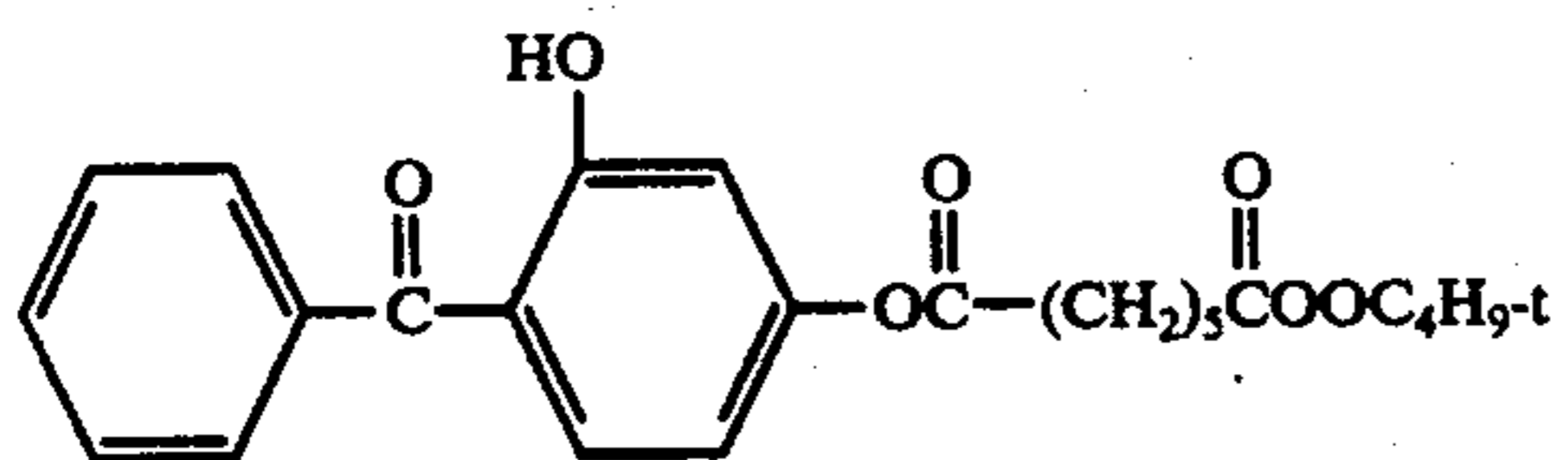
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wherein  $R_6$  is alkyl of 1-6 carbon atoms.

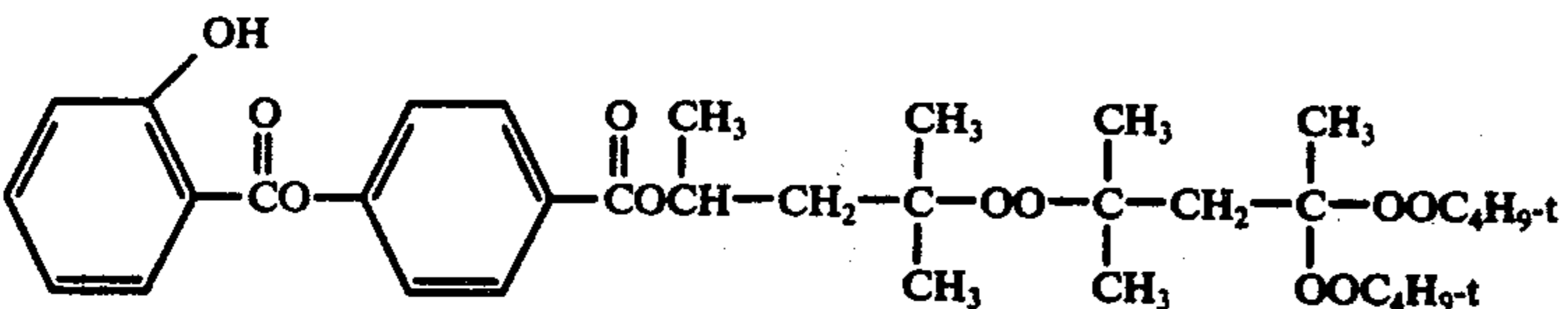
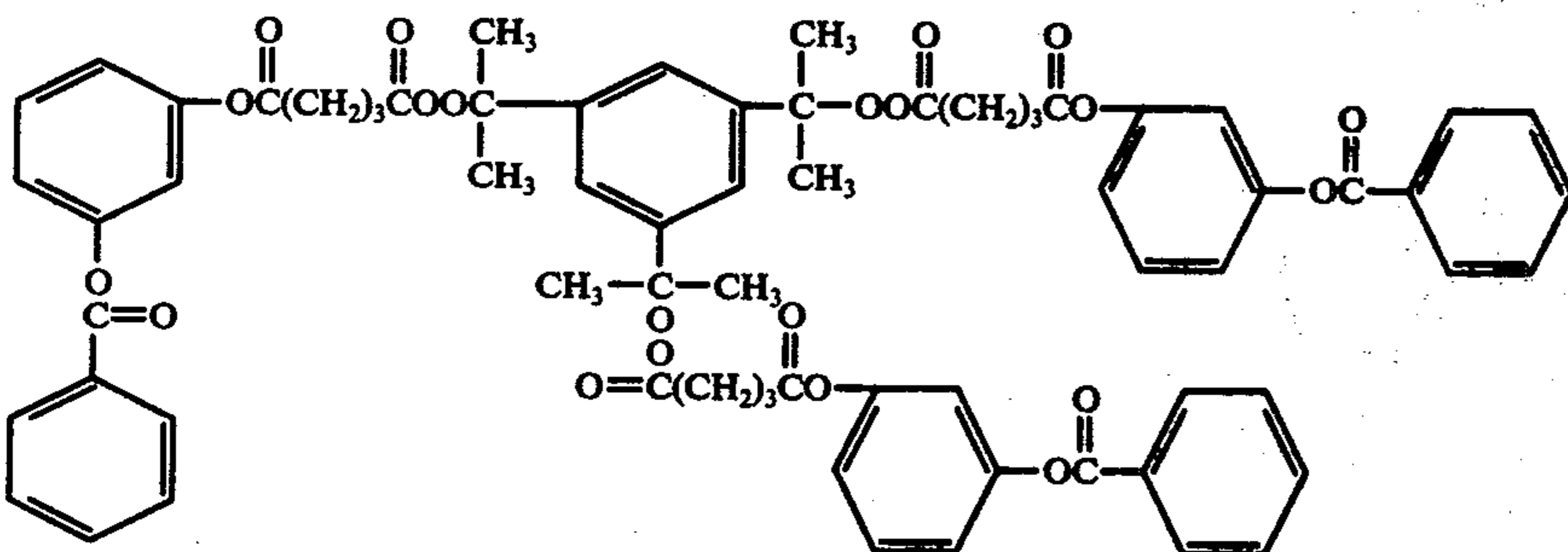
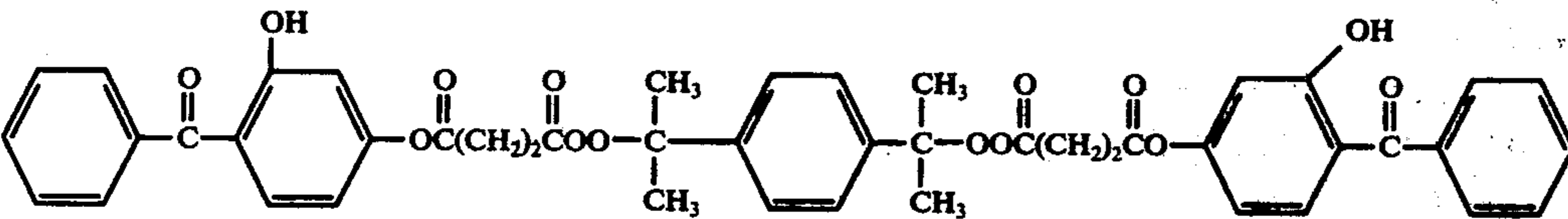
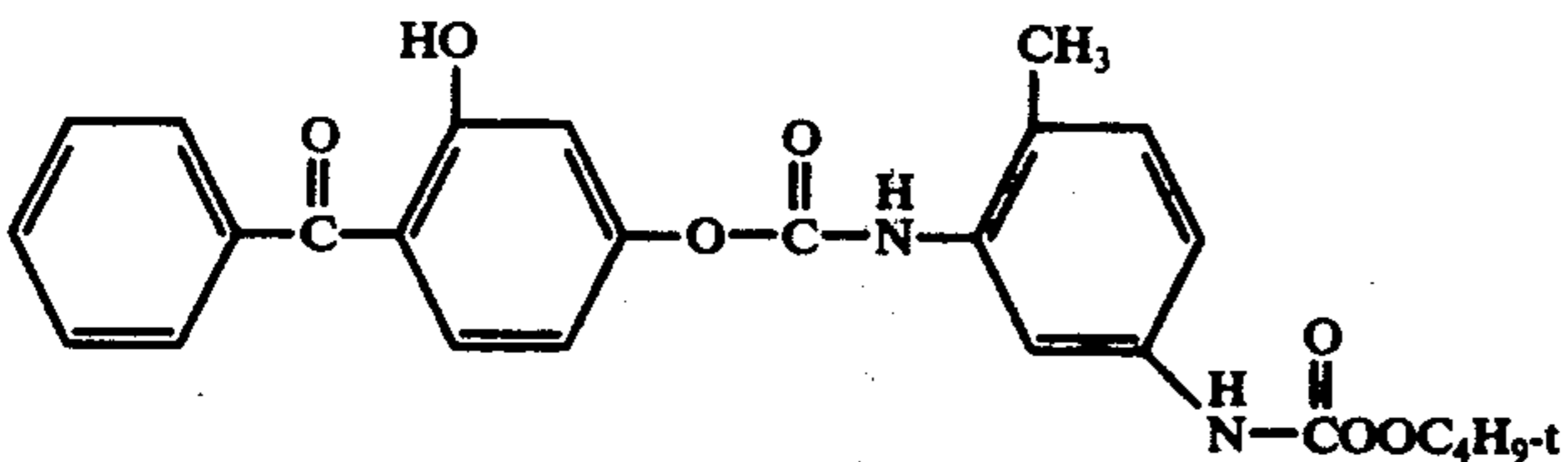
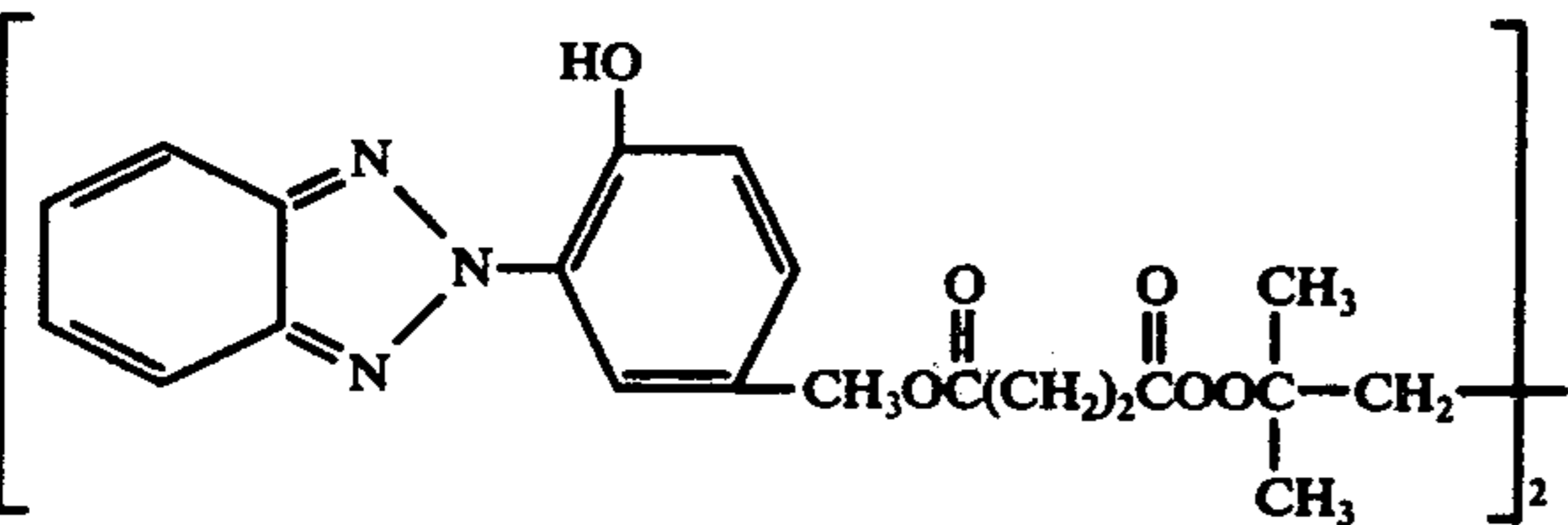
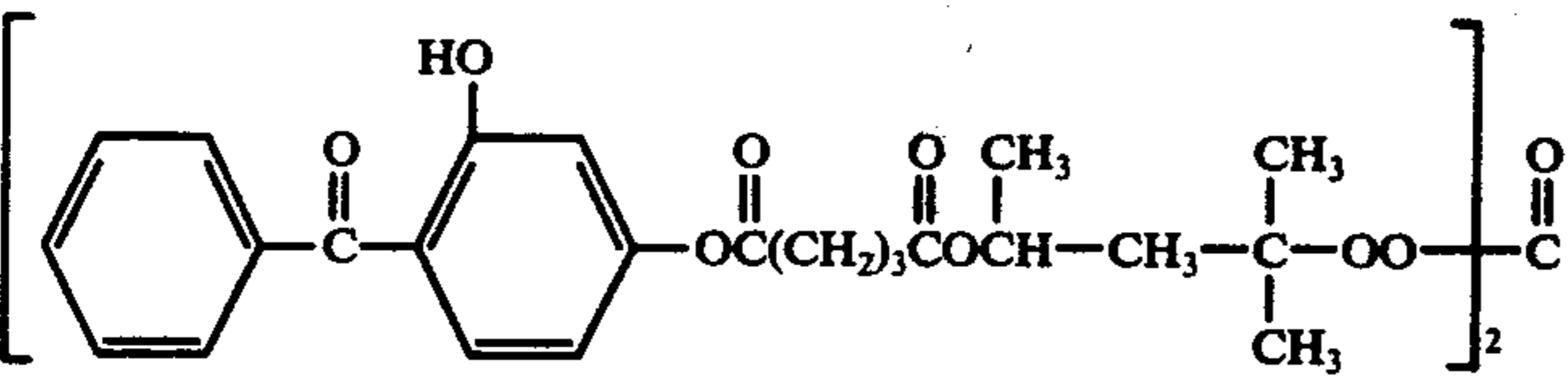
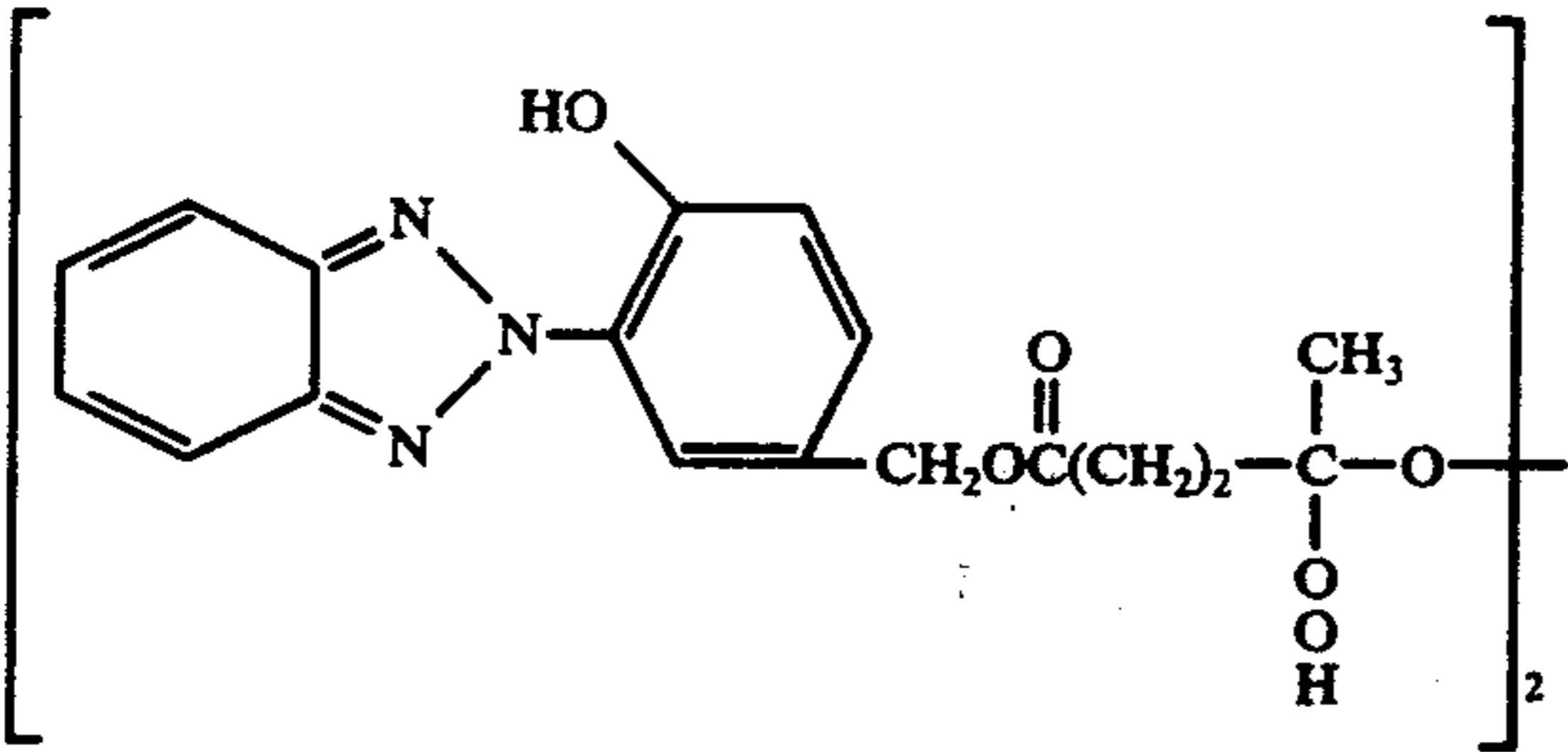
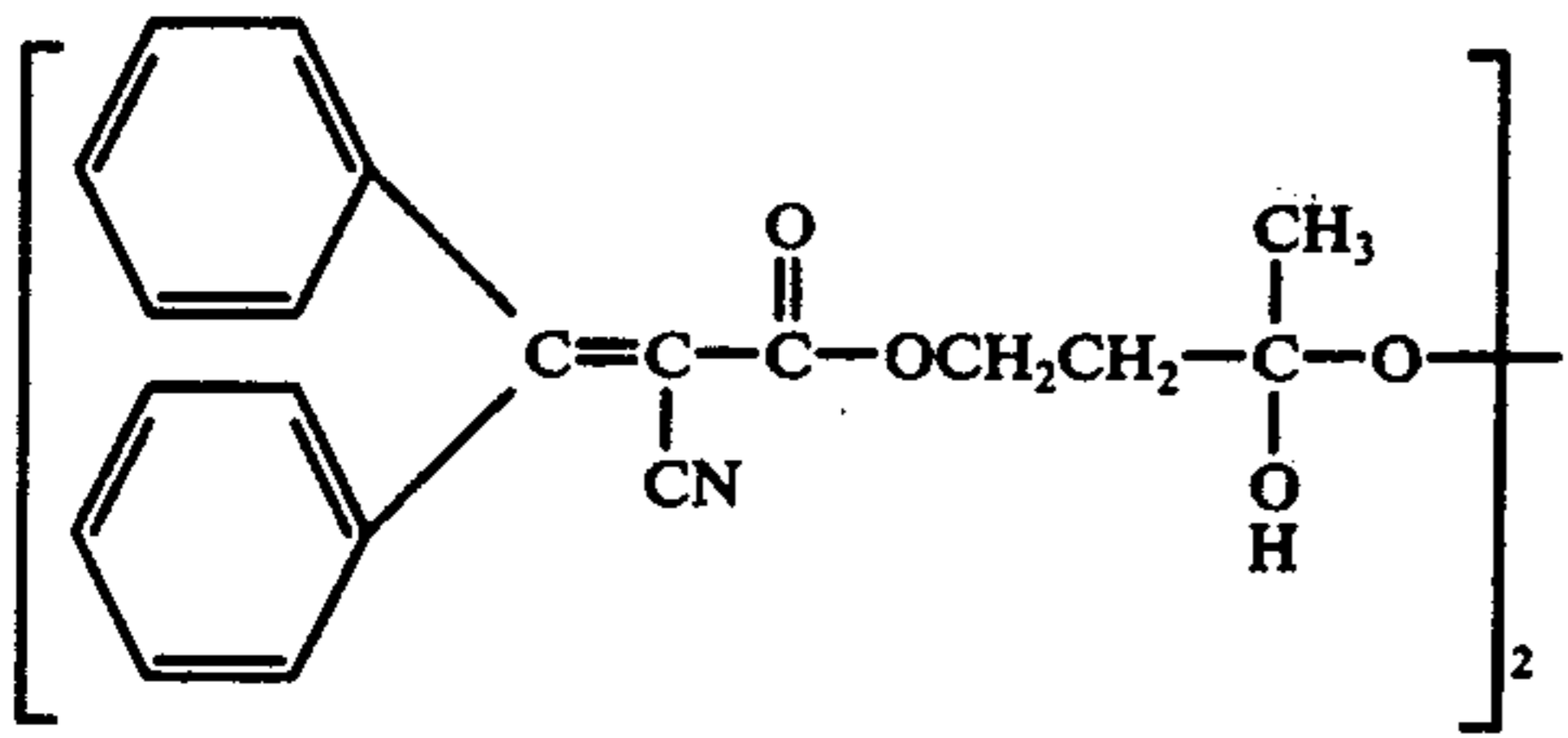
These compounds are of course employed in the form of a radical in the compounds of the present invention so that they are joined to another moiety containing a peroxide grouping or an azo grouping. The location of the juncture in the ultraviolet light stabilizing group is at a ring carbon or a carbon atom in the  $R_6$  group, usually through some coupling group such as an ester, amide, ether, sulfonate, carbonate, carbamate, etc.

Typical of the compounds of the present invention are the following:

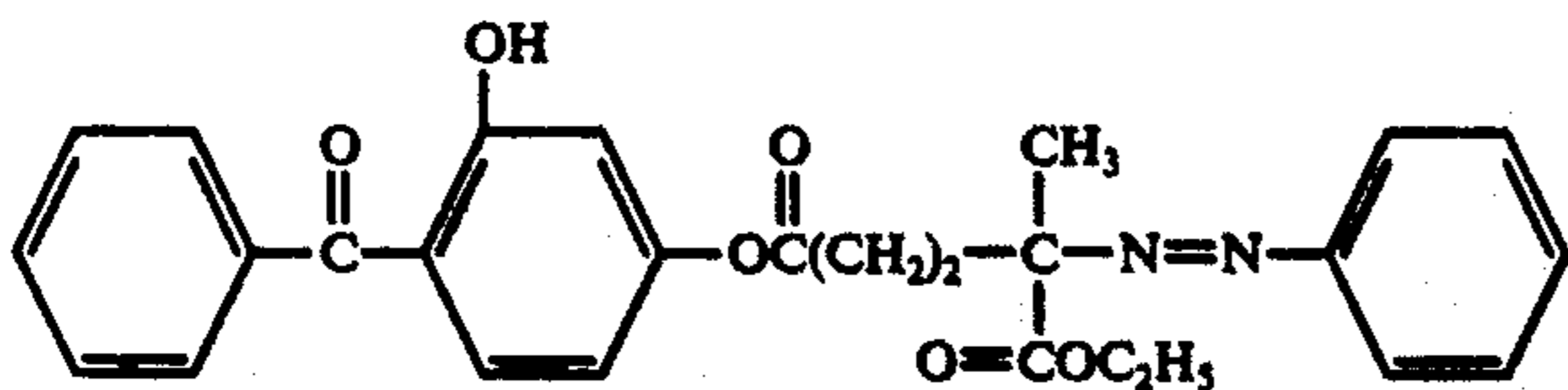
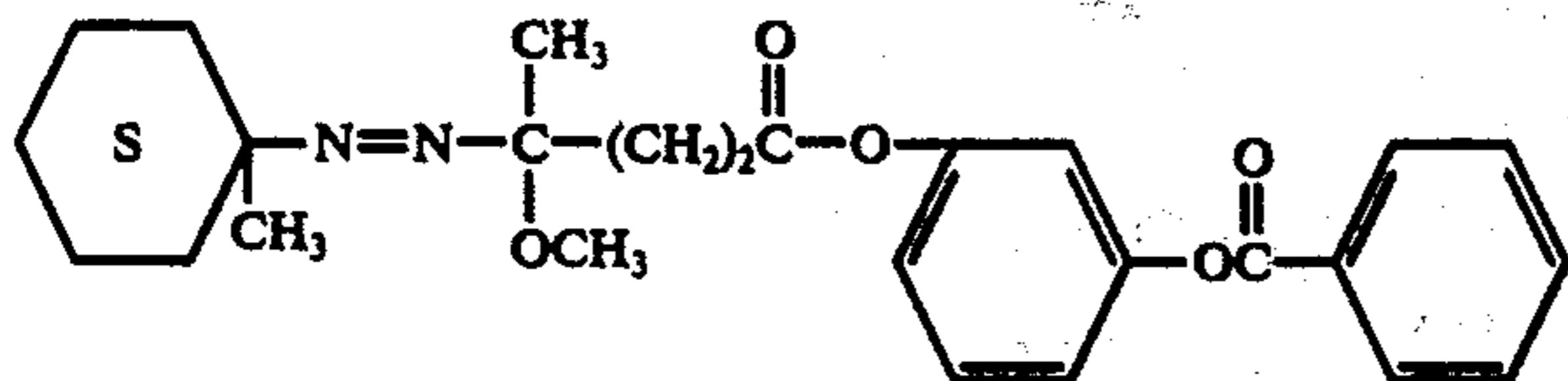
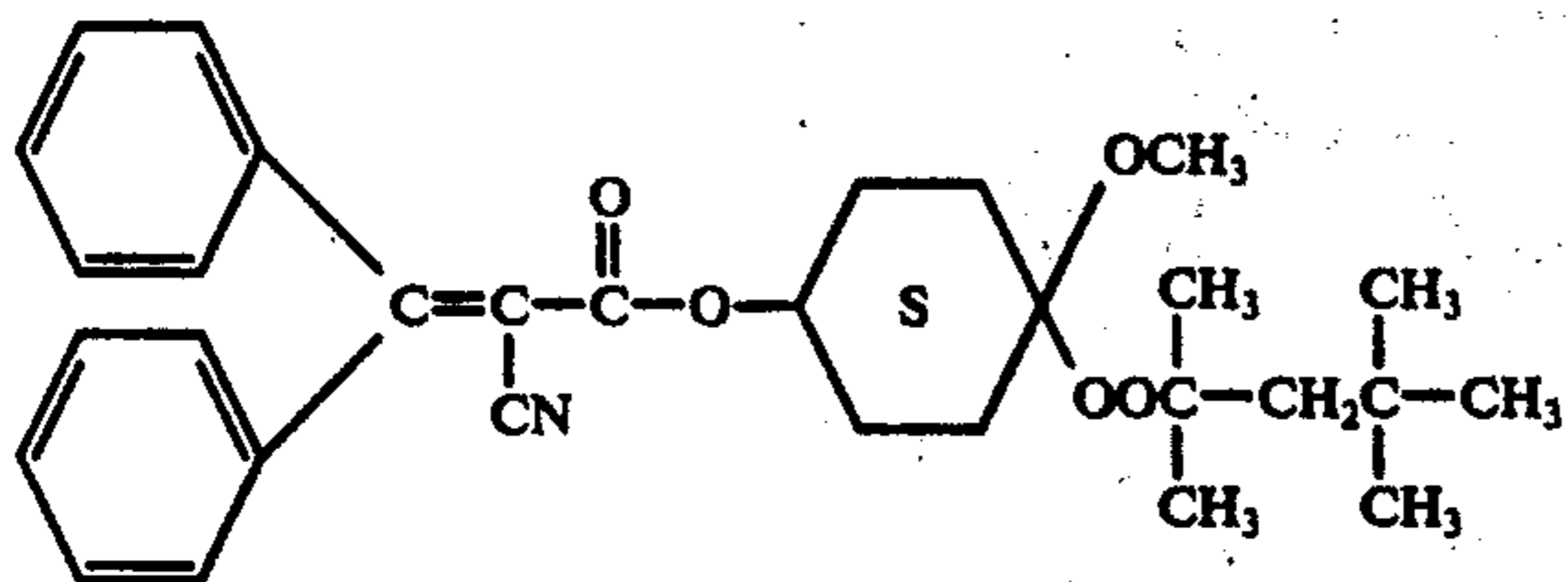
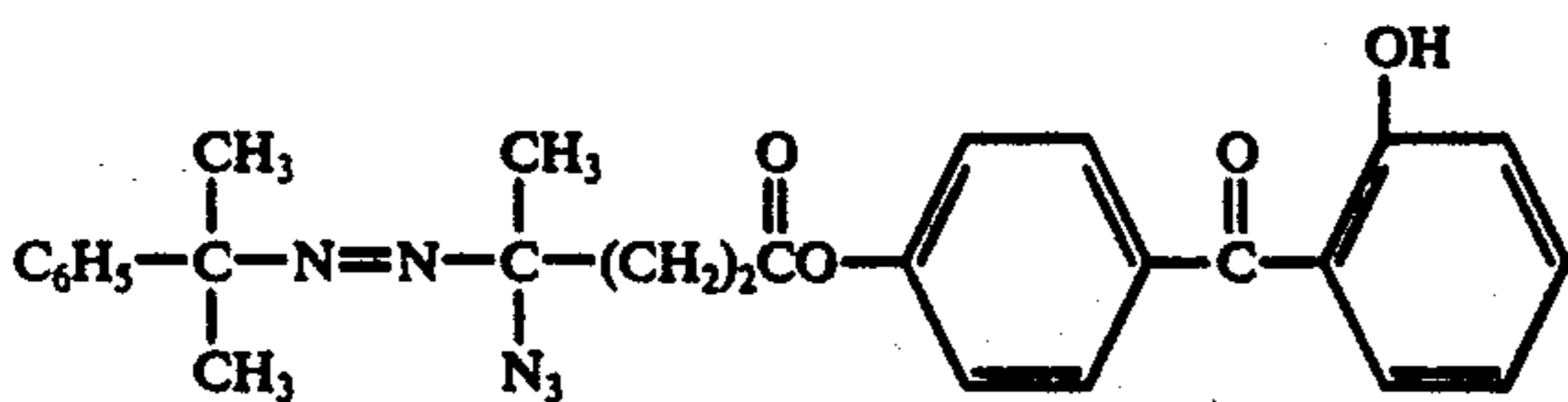
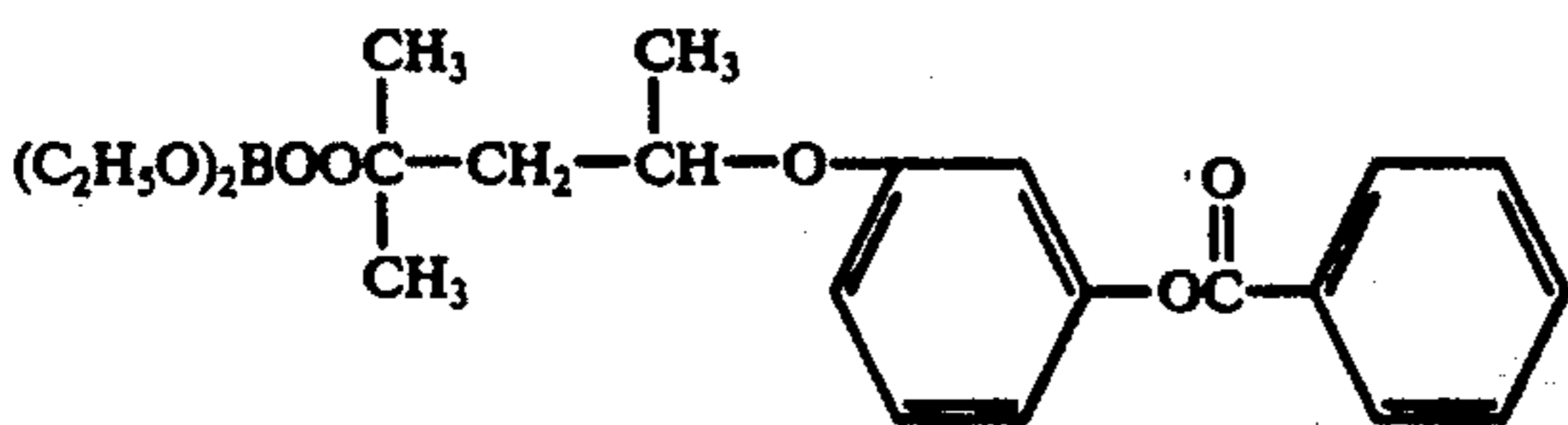
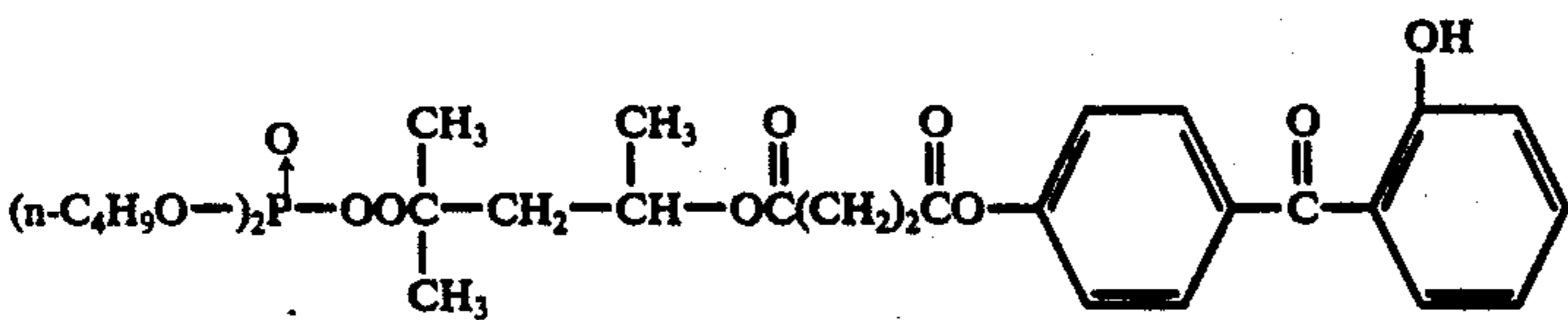
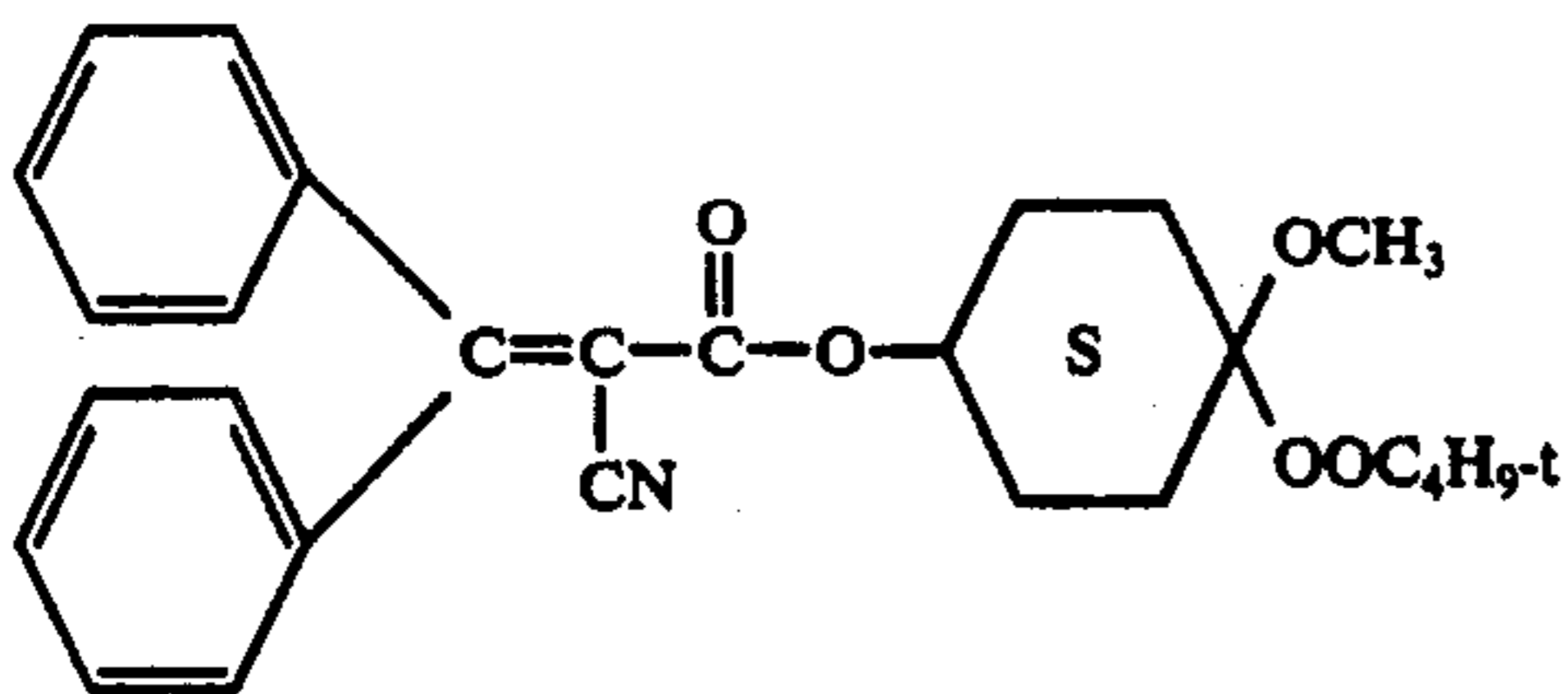
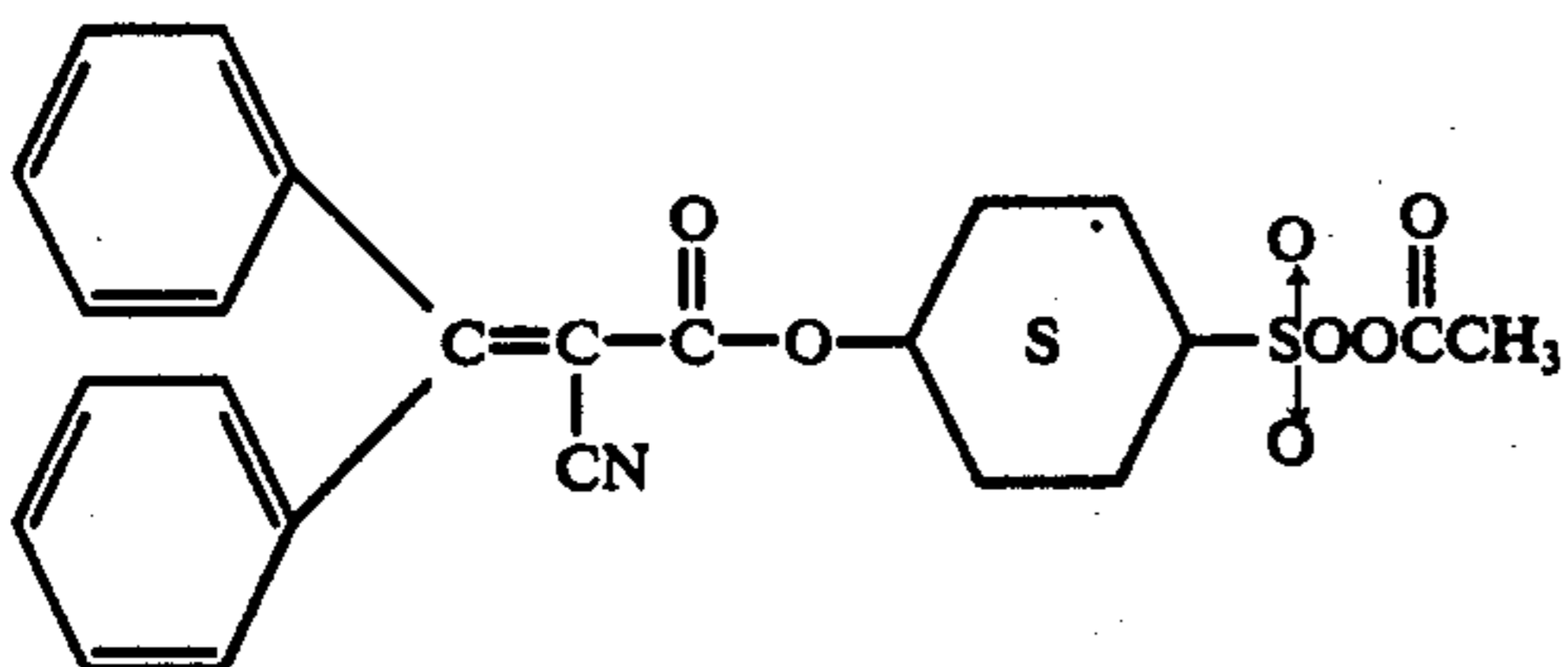
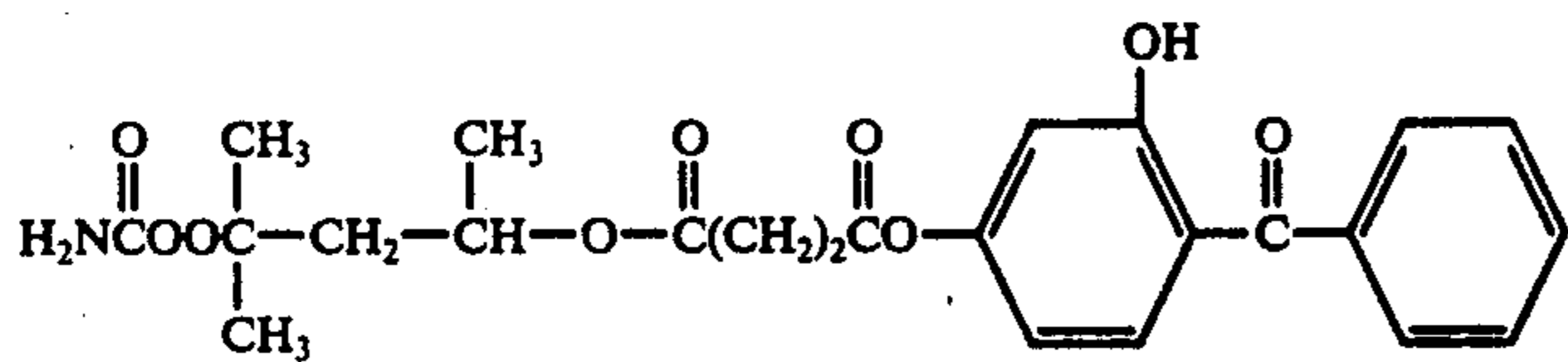




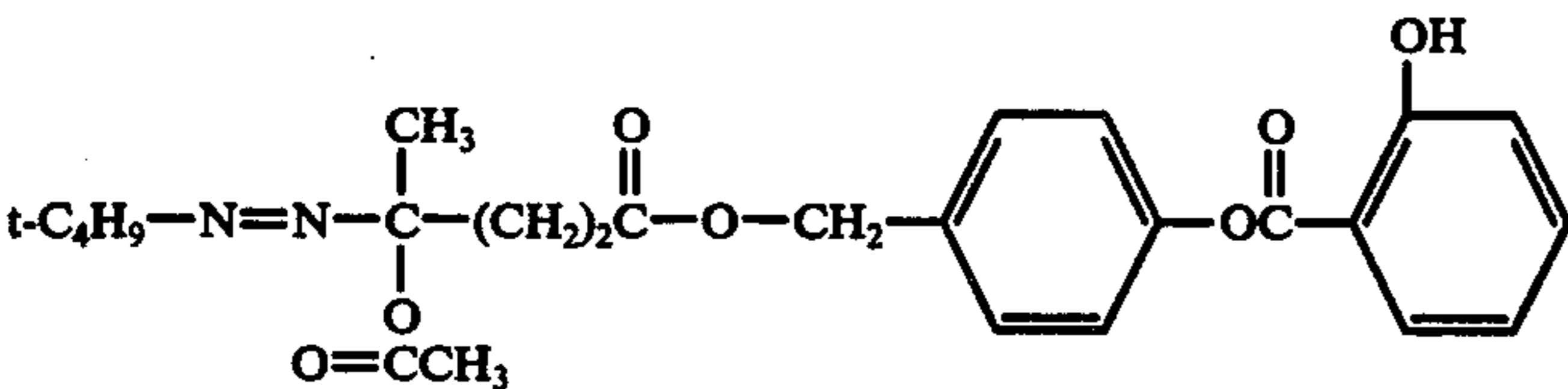
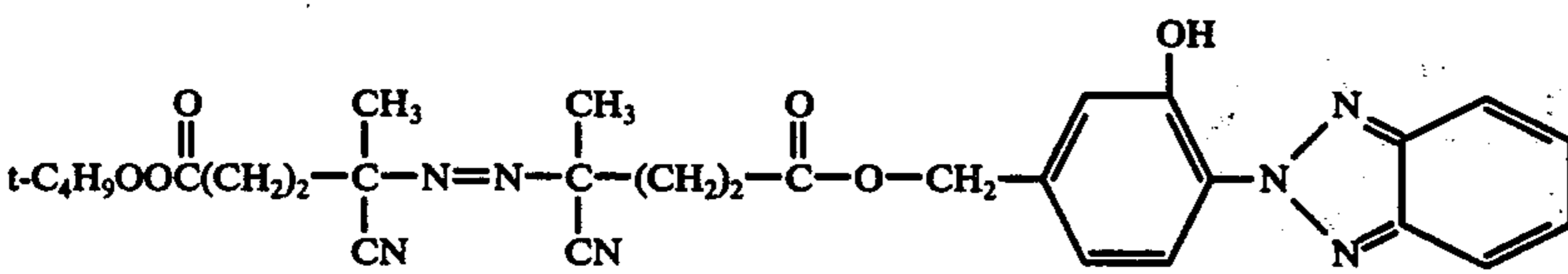
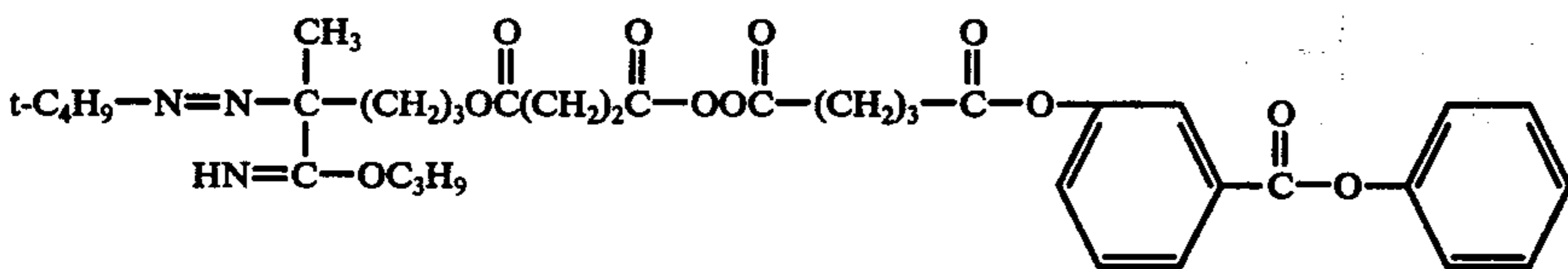
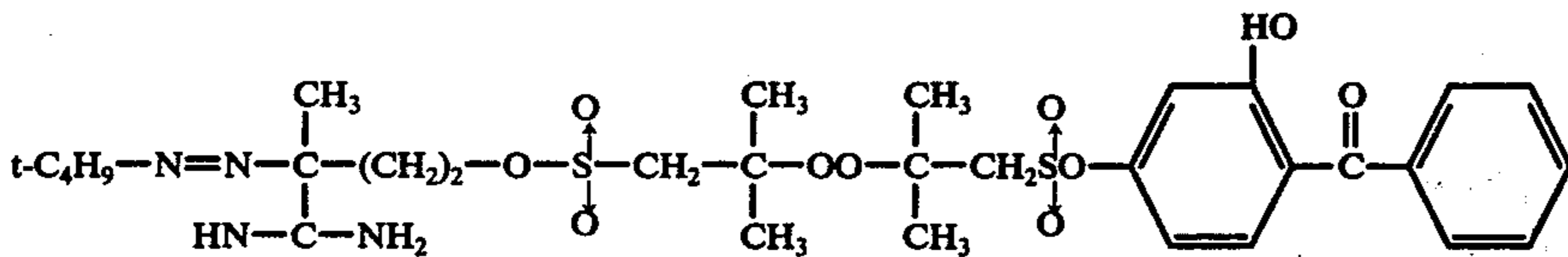
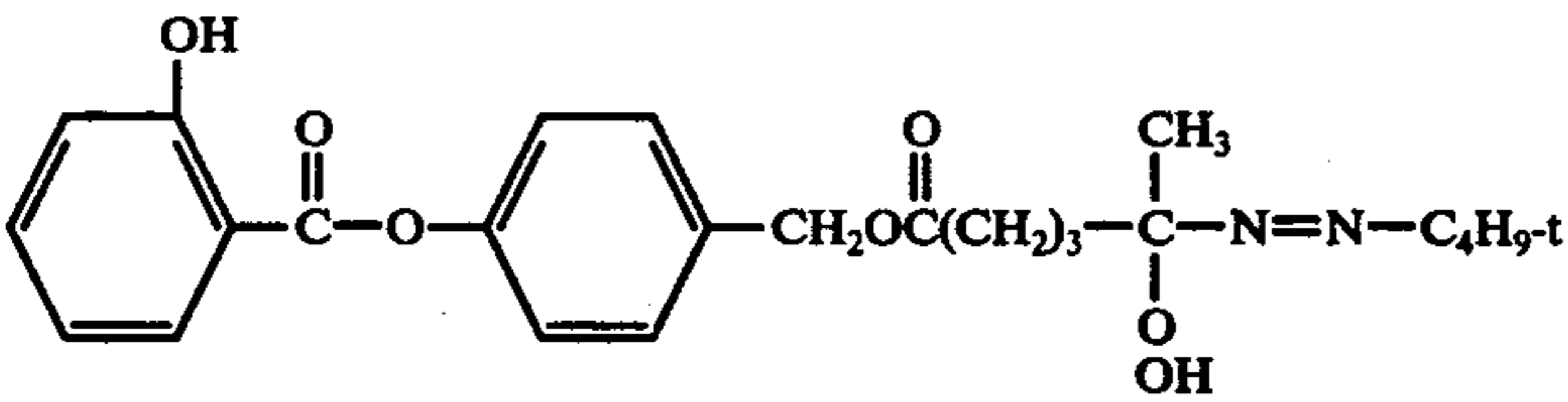
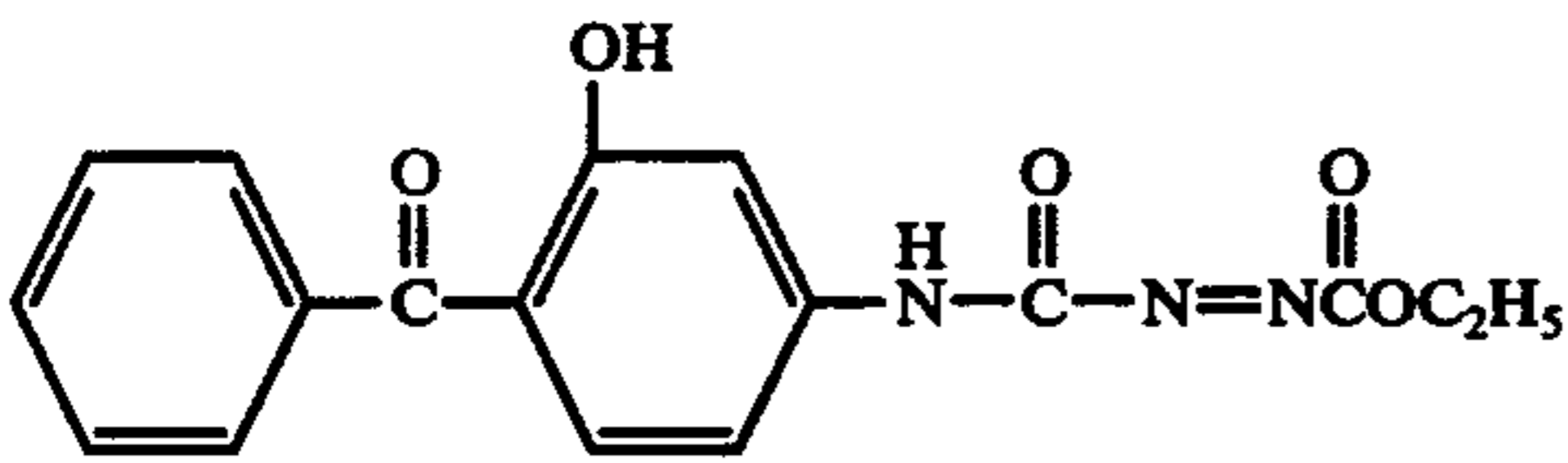
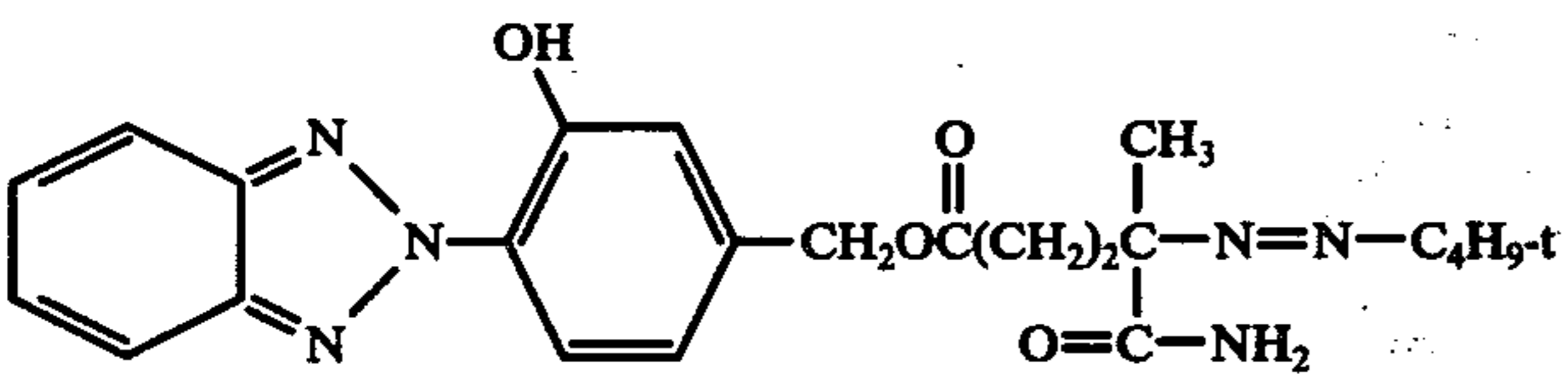
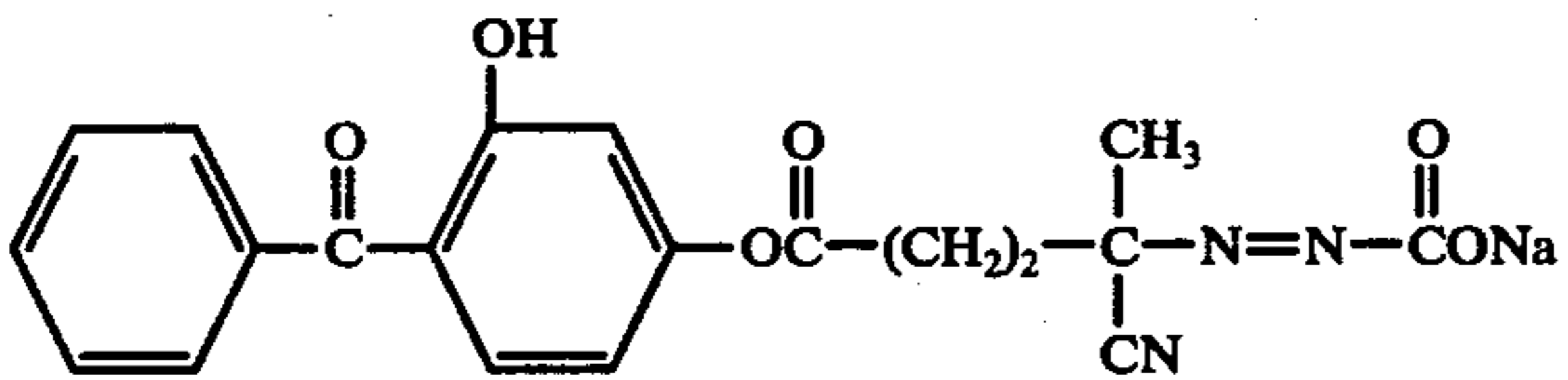
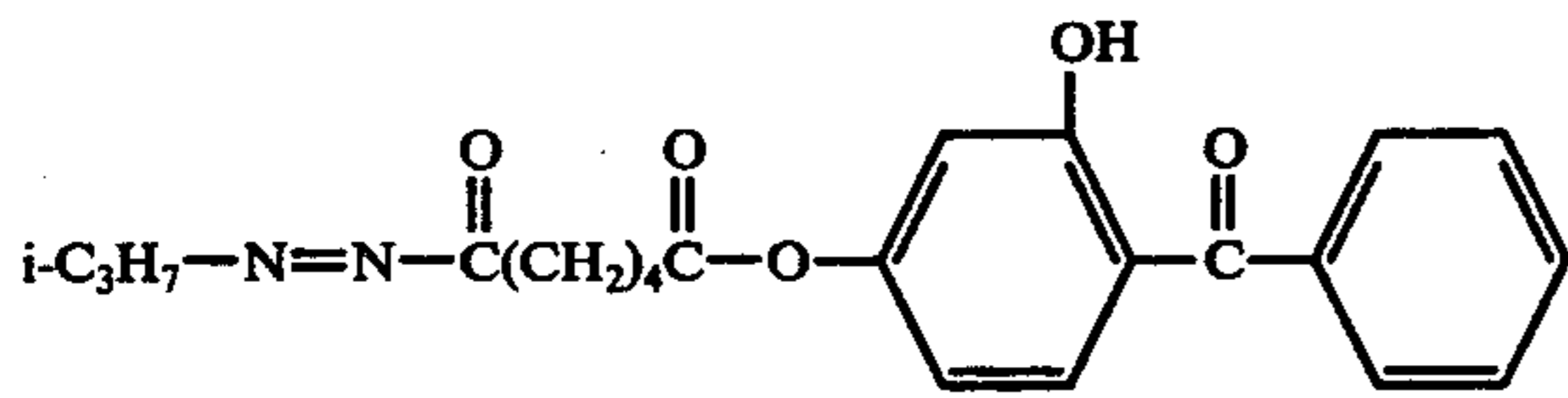
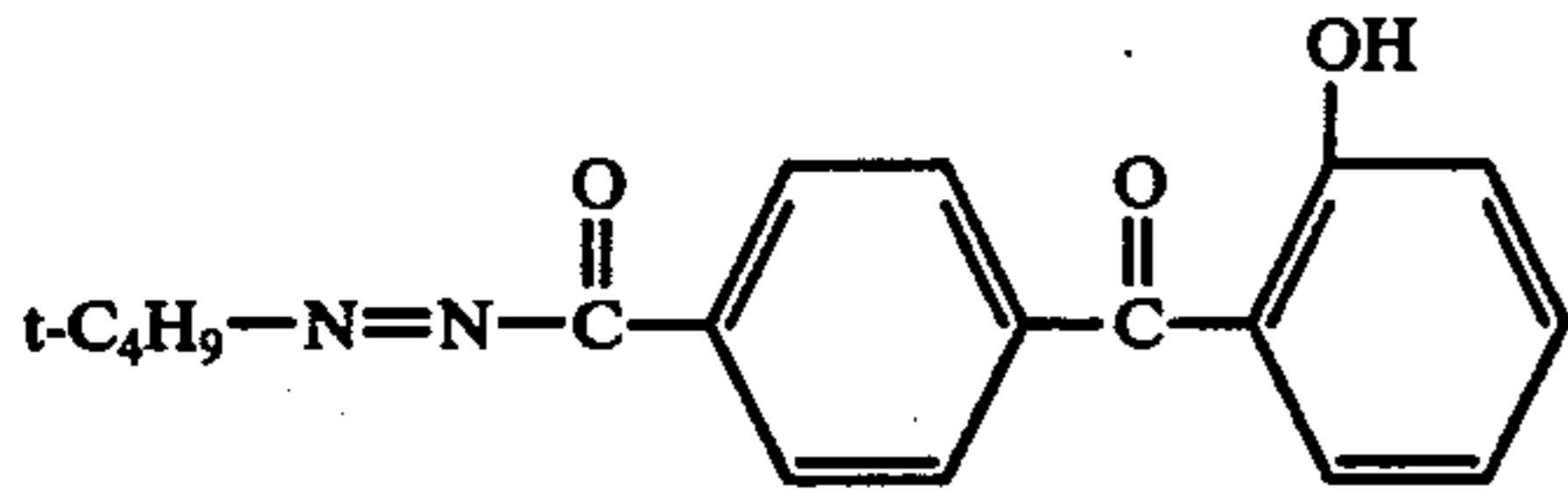
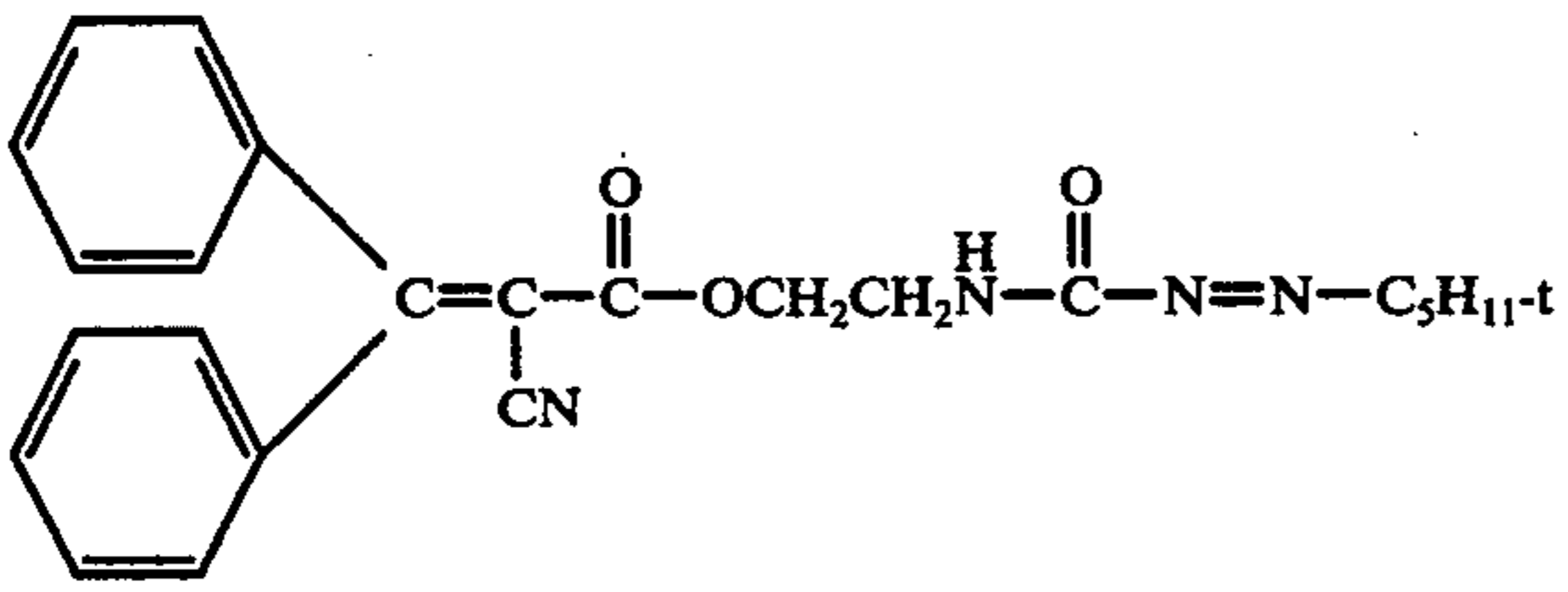
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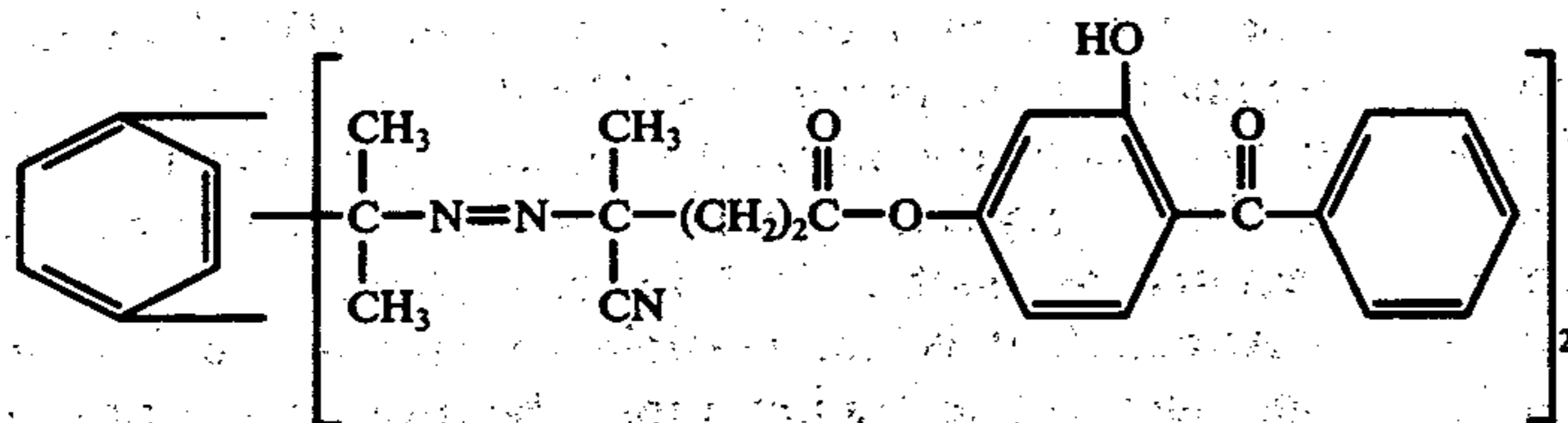
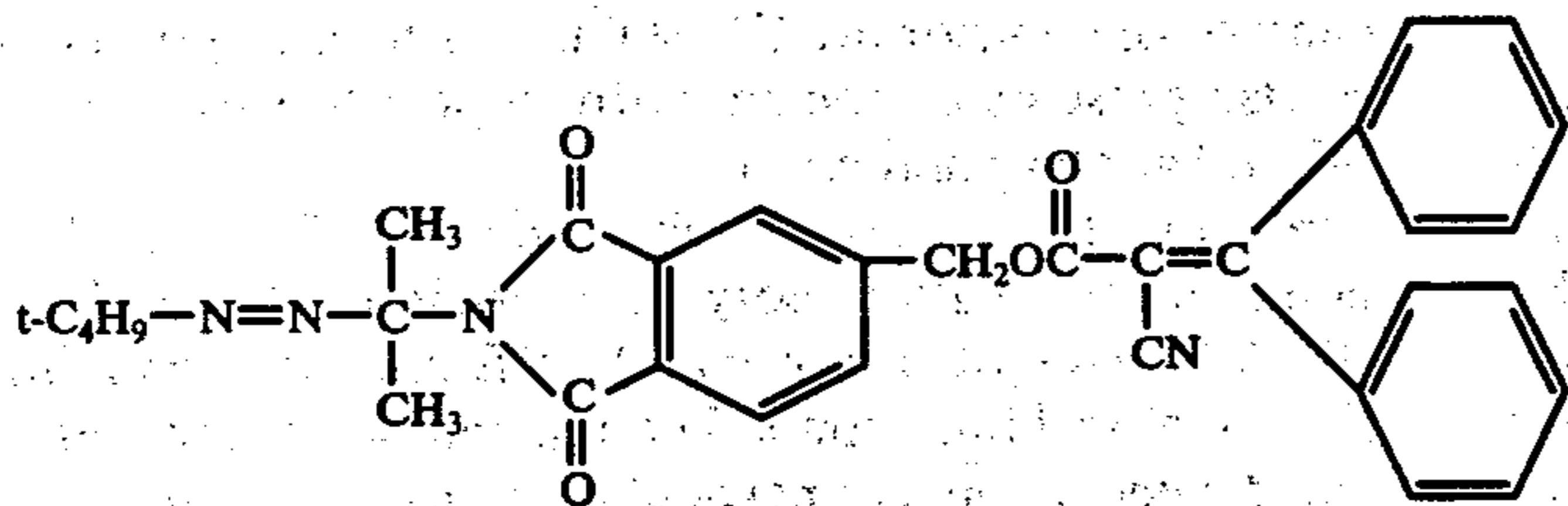
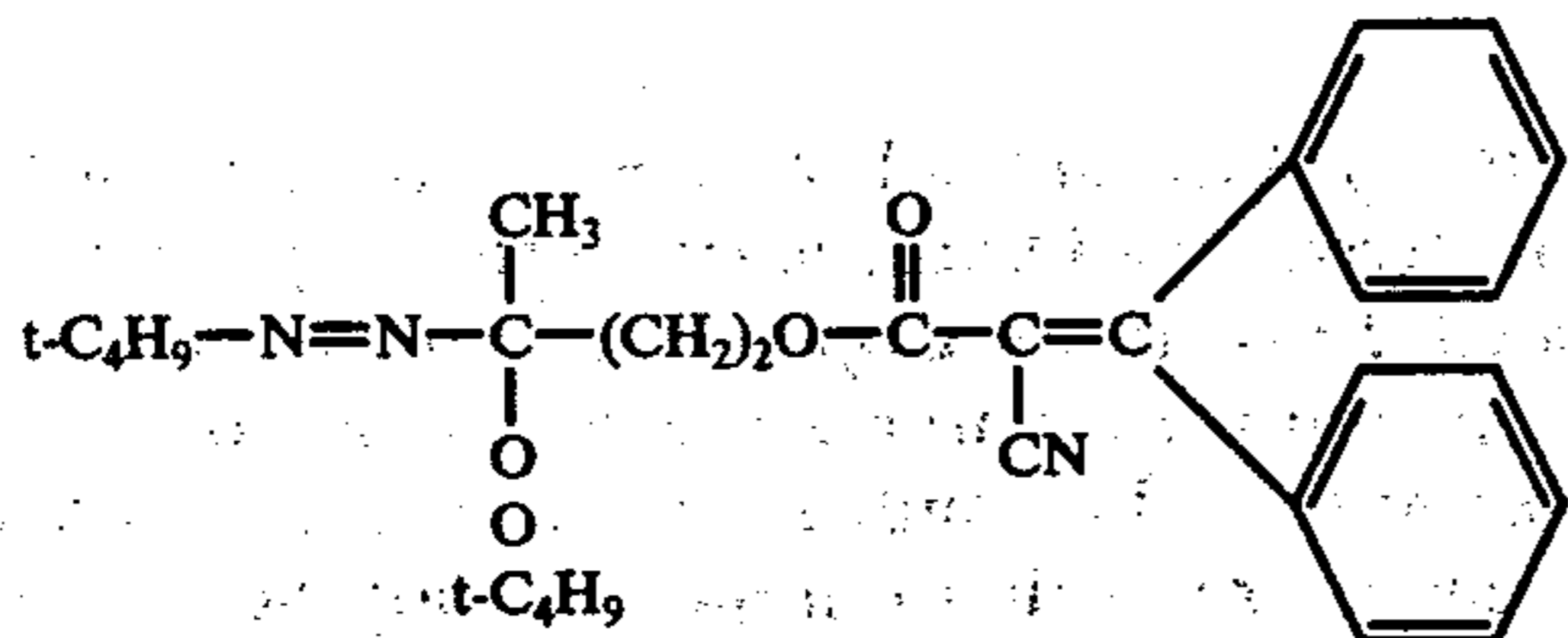
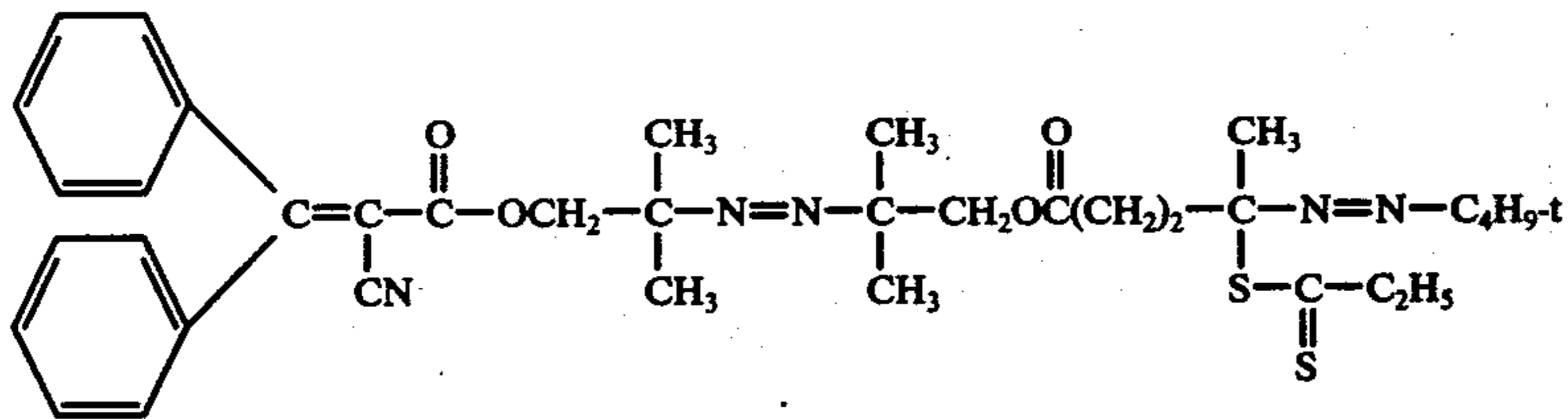
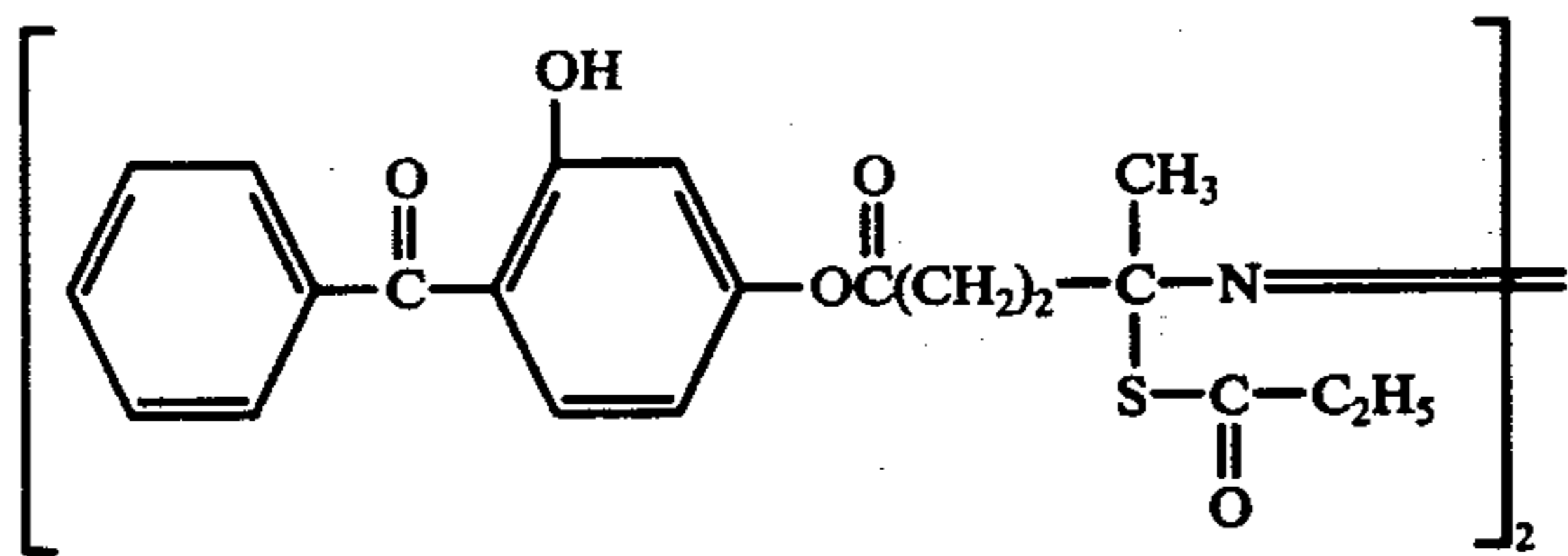
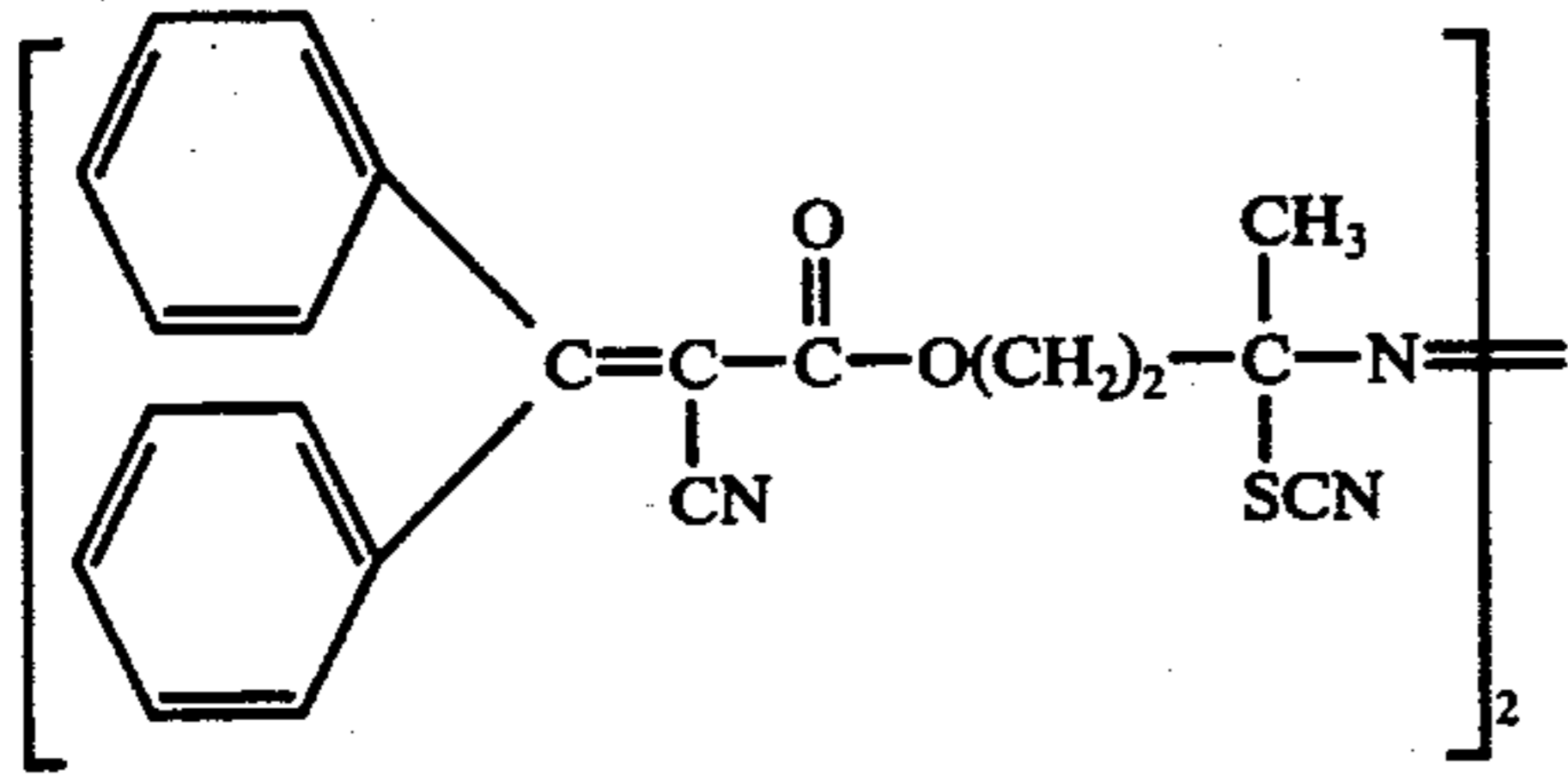
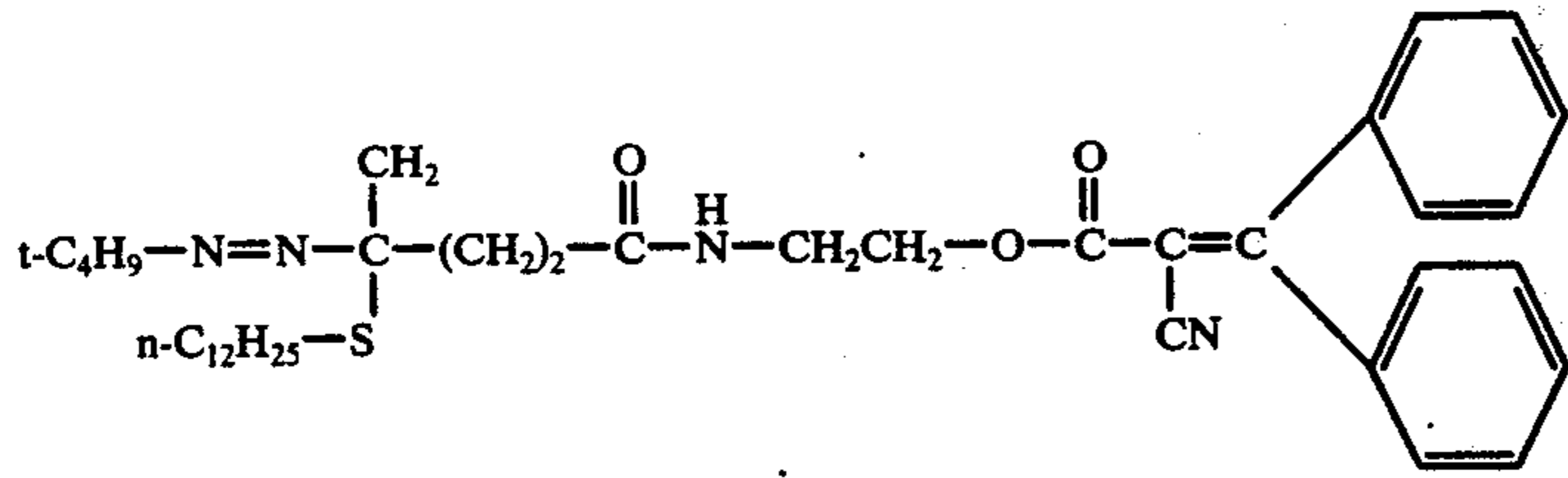
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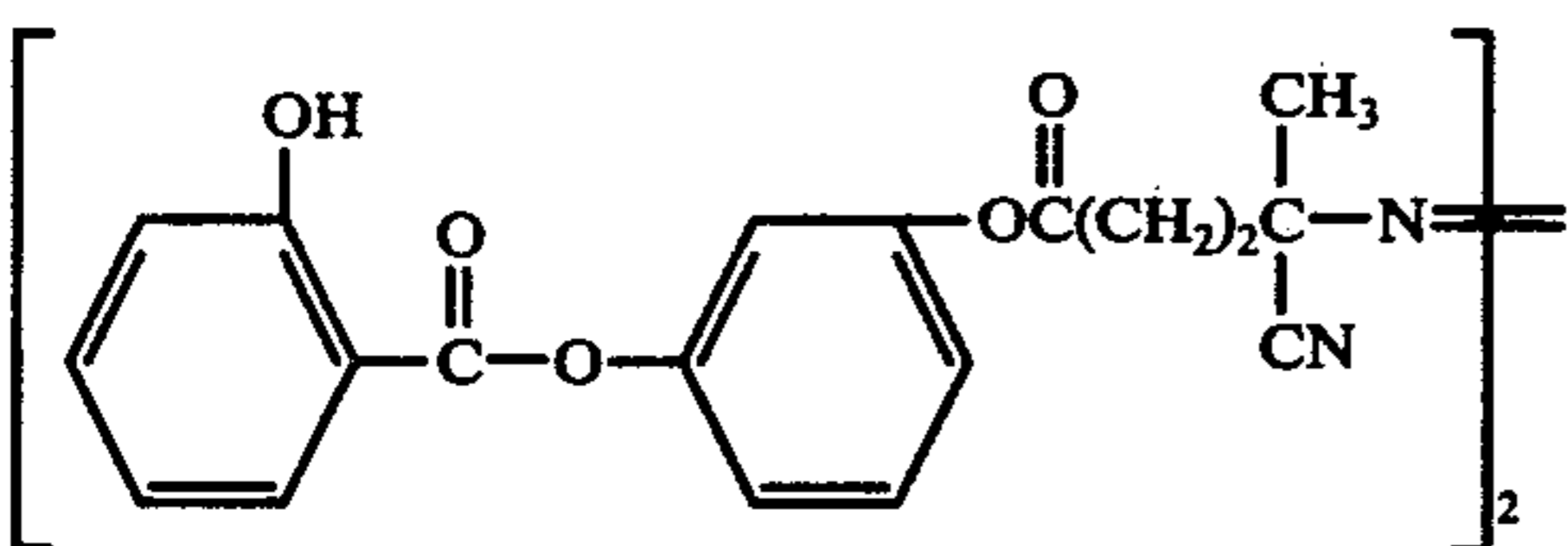
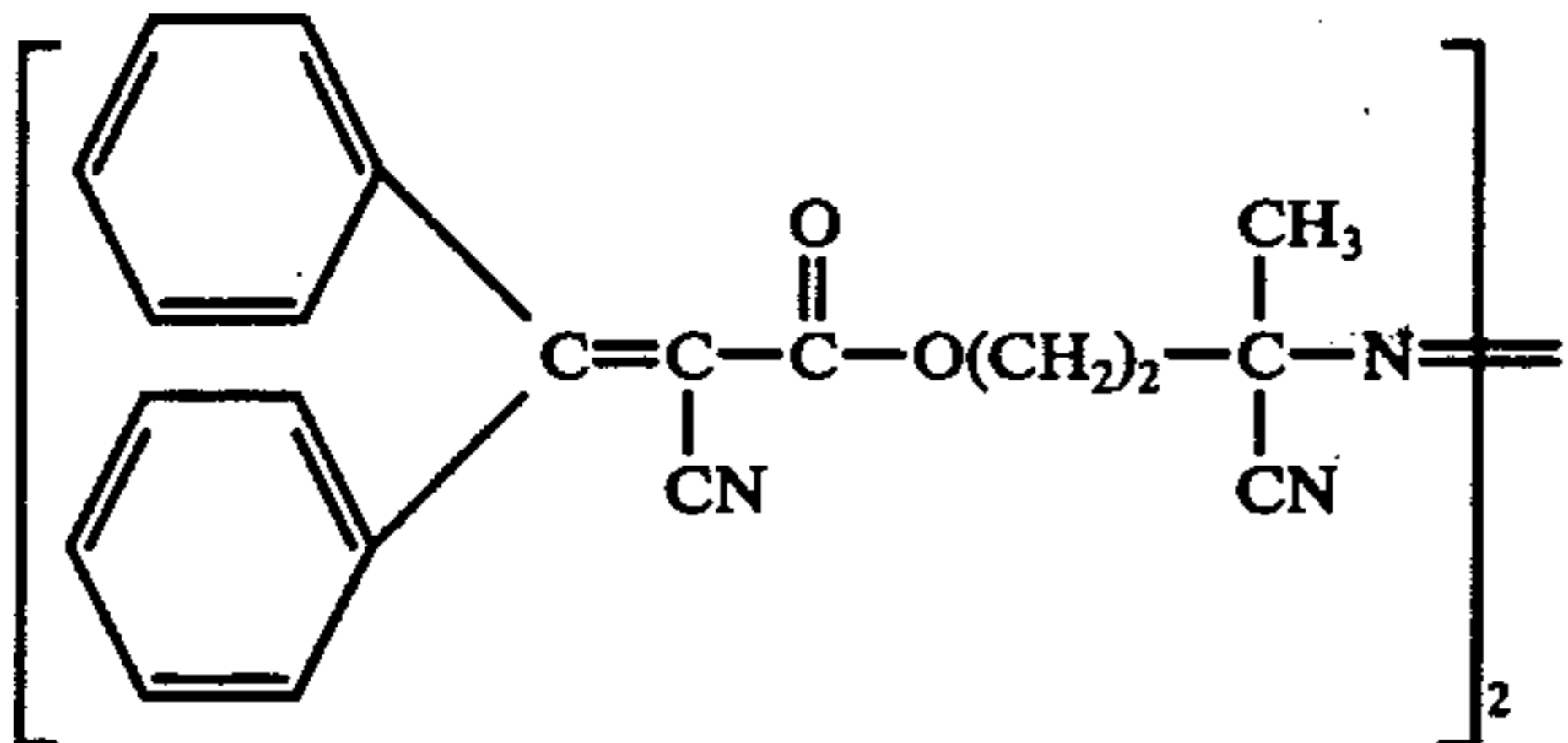
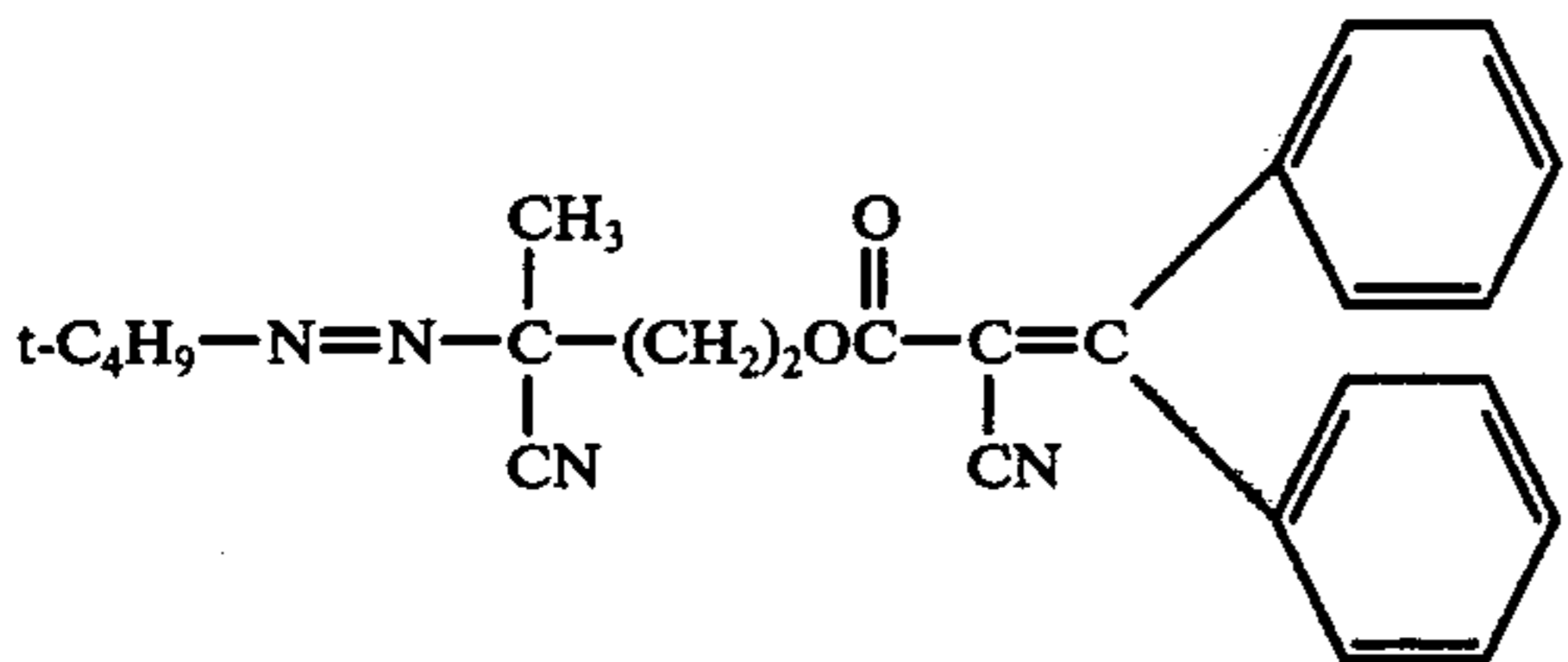
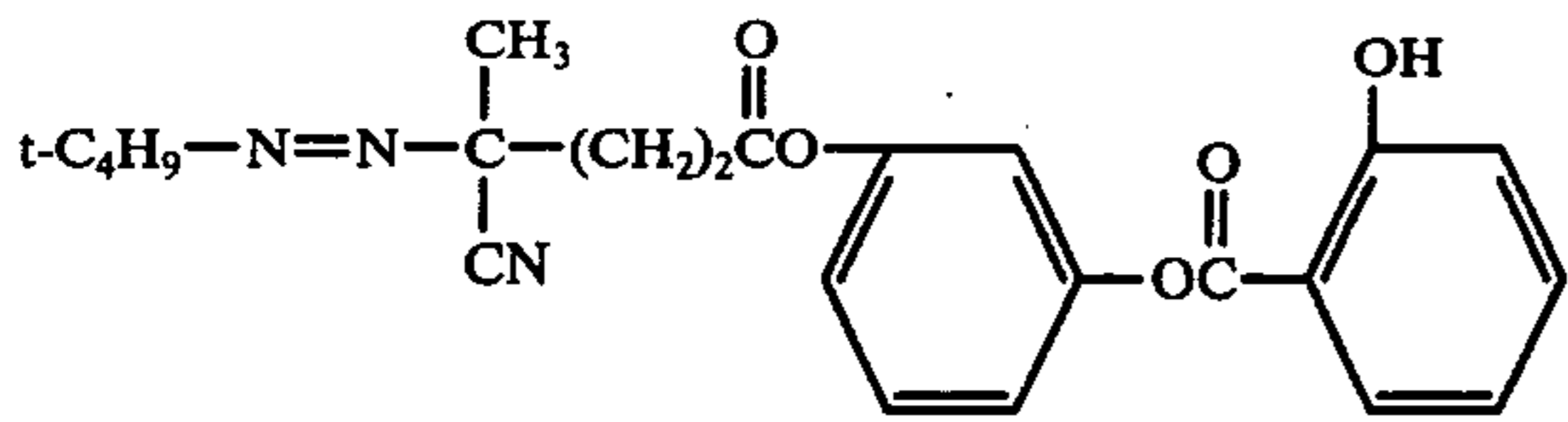
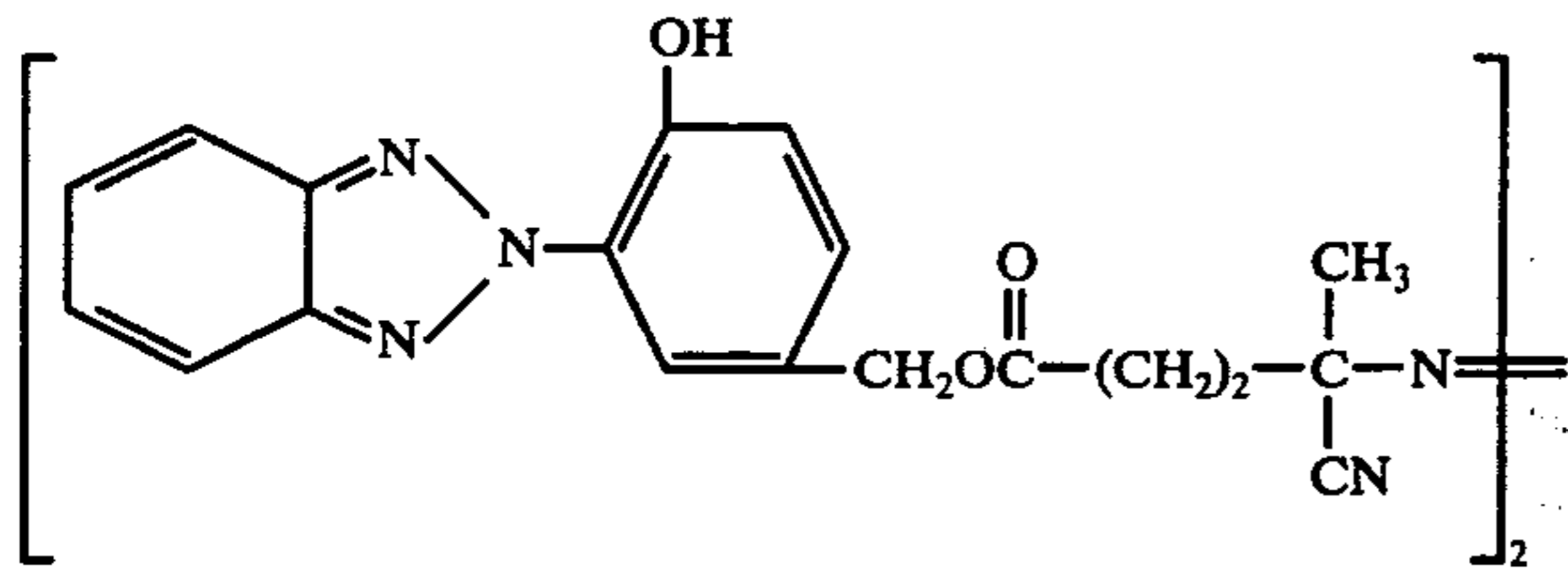
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The requirements of a good UV stabilizer are that it must absorb strongly in the 300 to 400 millimicron range (preferably in the 300-370 range); exhibit long-term stability toward UV light; it must dissipate the solar energy in such a manner as to cause no degradation or color development in the plastic; it must impart little or no color to the plastic material at the normal-use level; it must be heat stable and chemically inert. In addition the UV stabilizer must have good compatibility with the particular polymer it is to be used with; have low volatility; and be relatively non-toxic.

Many UV absorbers fulfill the first set of requirements. The second set of requirements will also be fulfilled if the UV absorber is directly attached to the polymer chain as is the case with the polymers made by this invention. In addition the UV absorber will not leach out in the presence of solvents. The UV absorber will be uniformly dispersed throughout the polymer and it will not migrate to or away from the surface on standing.

In addition, the polymers prepared from these novel initiators contain from  $\frac{1}{2}$  to 2 ultraviolet stabilizing groups per polymer chain, in contrast to the copolymers derived from the ethylenically unsaturated derivatives of phenyl salicylate and 2-hydroxybenzophenone mentioned in the prior art. None of the problems normally encountered in a copolymerization such as the adjustment of monomer ratios with reactivity ratios of the

monomers to get the desired composition of copolymer are encountered. In addition, many of the ethylenically unsaturated 2-hydroxybenzophenone and phenyl salicylate derivatives of the prior art tend to homopolymerize preferentially. Difficulties are also encountered when attempts are made to prepare homogeneous copolymers with monomers of lesser reactivity such as vinyl chloride and vinyl acetate. The ease with which many of these prior art UV stabilizers tend to polymerize also presents a problem with respect to their preparation, handling and storage.

In order to effectively withstand the effects of UV radiation the resultant polymers should contain at least 0.01% by weight of the initiating fragment containing the UV absorbing group. The maximum concentration will depend upon the particular monomer being polymerized and the specific end use of the polymer. In most cases a concentration of 2.0% of the UV absorbing fragment on the polymer will be the maximum concentration necessary unless the resultant polymer is to be used as a very thin coating, in which case more will be required, as much as 10% in some cases.

Although it is not possible to narrowly define an optimum concentration range because the exposure conditions of the polymers (such as degree of protection required, polymer thickness, etc.) vary considerably, a

concentration range of 0.1 to 2.0% by weight will suffice for most applications. Each of the different polymers requires a certain concentration range of UV stabilizer for optimum protection because all of the polymers do not have the same susceptibility to degradation by UV. Table I shows some of the concentration ranges of UV absorber that are presently used for various polymers.

TABLE I

Concentration Ranges for UV Stabilizers	
Polymer	Concentration, % (wt.)
polyacrylics	≤0.01
polyethylene	0.01 - 1.0
unsaturated polyesters	0.1 - 2.0
polystyrene	0.2 - 0.5
cellulosics	0.2 - 2.0
poly (vinyl chloride)	0.25 - 1.0
polypropylene	0.5 - 2.0
coatings	0.1 - 5.0

The polymers of this invention may be prepared from the novel free radical polymerization initiators by any of the usual free radical polymerization techniques, i.e. bulk, suspension, solution, or emulsion polymerization

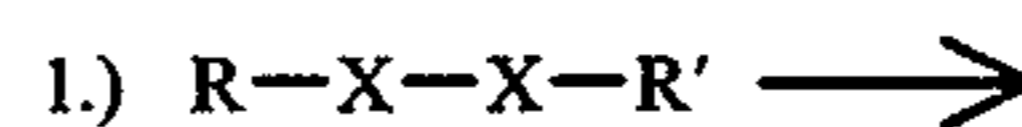
The polymers of this invention may be prepared from the polymerization and copolymerization of ethylenically unsaturated monomers at suitable temperatures and pressures that are polymerizable by free radicals. Such monomers are well known in the art as taught for example in "Encyclopedia of Polymer Science and Technology, Plastics, Resins, Rubbers, Fibers" Volume 7 pages 361-431, Interscience Publishers, 1967. The ethylenically unsaturated monomers include:

- a. Olefins, such as ethylene, propylene, styrene, alpha-methylstyrene, chlorostyrene, vinyltoluene, vinyl pyridine and divinylbenzene
- b. Diolefins, such as 1,3-butadiene, isoprene and chloroprene
- c. Vinyl esters, such as vinyl acetate, vinyl propionate, vinyl laurate, vinyl benzoate and divinyl carbonate
- d. Unsaturated nitriles, such as acrylonitrile and methacrylonitrile
- e. Acrylic acid, Methacrylic acid and their esters and amides, such as methyl, ethyl, n-butyl and 2-ethylhexyl acrylates and methacrylates, and acrylamide and methacrylamide
- f. Maleic anhydride
- g. Maleic and fumaric acids and their esters
- h. Vinyl halo and vinylidene halo compounds, such as vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride and vinylidene fluoride
- i. Perhalo olefins, such as tetrafluoroethylene, hexafluoropropylene and chlorotrifluoroethylene
- j. Vinyl ethers, such as methyl vinyl ether, ethyl vinyl ether and n-butyl vinyl ether
- k. Allyl esters, such as allyl acetate, allyl benzoate, diallyl phtaalate, allyl ethyl carbonate, triallyl phosphate, diallyl fumarate and diallyl carbonate
- l. Acrolein
- m. Methyl vinyl ketone
- n. and mixtures thereof

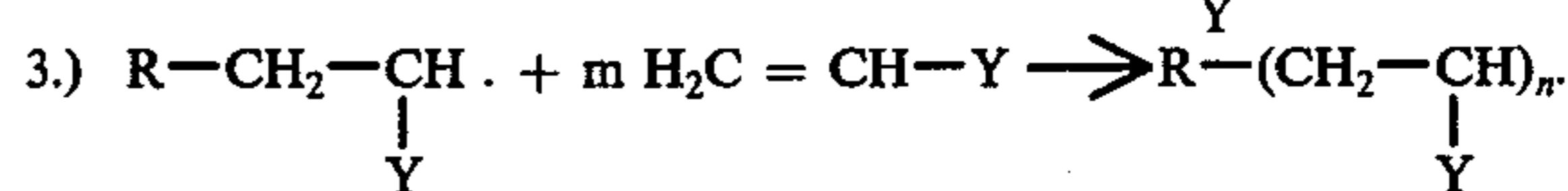
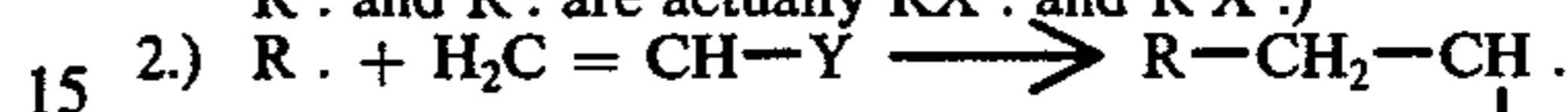
The polymerizations using these novel initiators may be carried out from below  $-20^{\circ}\text{C}$  to above  $200^{\circ}\text{C}$  depending on the peroxide or azo structure of the initiator and the monomer employed. Generally the polymerizations will be carried out between  $50^{\circ}$  to  $100^{\circ}\text{C}$  depending of the half-life of the initiator used and the

vinyl monomer being polymerized. Some free radical ethylene polymerizations are carried out above  $200^{\circ}\text{C}$ .

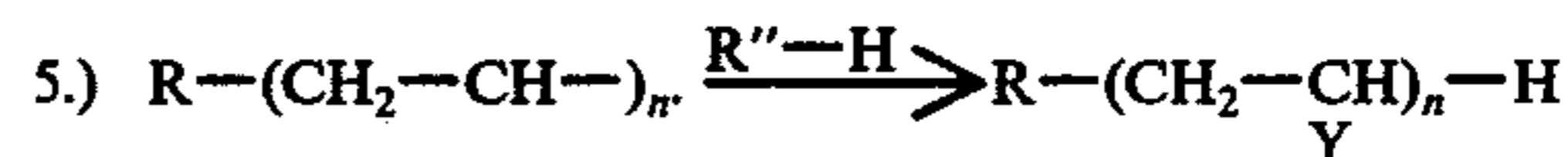
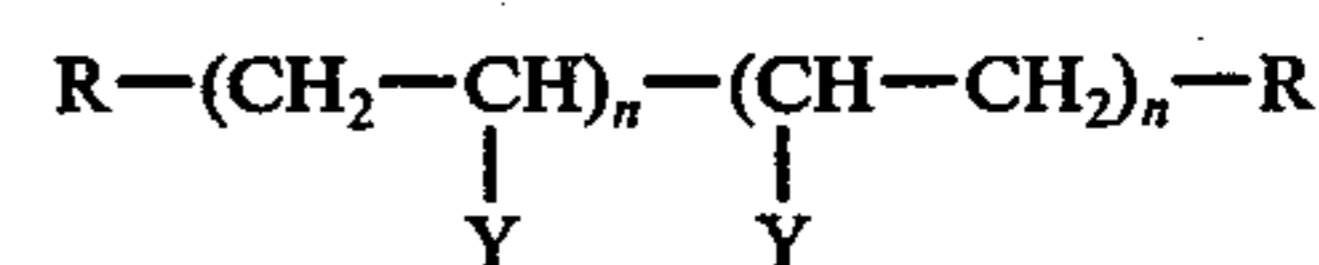
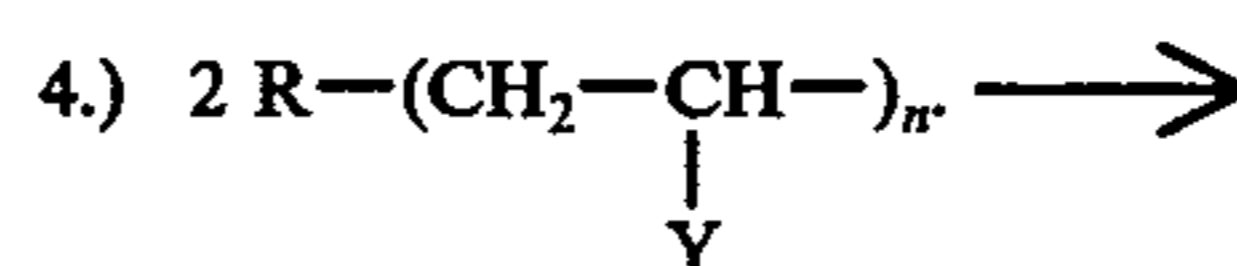
When initiators of the present invention are used to polymerize or copolymerize vinyl monomers, they first fragment into free radicals (equation 1) which then add to a vinyl monomer to form a new free radical (equation 2) which subsequently adds to more vinyl monomer and so on to form the growing polymer chain (equation 3):



R. + R'. (when  $-\text{X}-\text{X}-$  is  $-\text{O}-\text{O}-$ , then R. and R'. are actually  $\text{RX} \cdot$  and  $\text{R}'\text{X} \cdot$ )



With some monomers, e.g. butadiene and styrene, the growing polymer chains terminate predominantly by coupling (equation 4) while with others the termination reaction may be by disproportionation of two growing polymer chains, hydrogen abstraction or chain transfer (e.g. equation 5):



Thus, it can be seen that when both R and R' contain UV stabilizing groups, i.e. when symmetrical initiators of the present invention are used each polymer chain will contain from one to two UV stabilizing groups, and that when only R contains a UV stabilizing group, i.e. when unsymmetrical initiators are used, only one half of the polymer chains will be initiated by a free radical containing a UV stabilizing group. In this case only one half of the polymer chains will contain UV stabilizing groups on the average.

Thus, one method of controlling the concentration of UV stabilizer in the polymer is the choice of using a symmetrical vs. unsymmetrical initiator of the present invention. This, of course, has to be correlated with the molar initiator requirements required in order to obtain the desired molecular weight of polymer at the desired temperature in the specified time period, which, in turn, varies with each monomer and comonomer system and is well known to the art.

Other methods of controlling the concentration of UV stabilizer in the polymer of copolymer is to use a conventional initiator in conjunction with the initiators of the present invention or to use initiators of the present invention of suitable molecular weight or to use initiators of the present invention that contain more than one ultraviolet absorbing group in both R and R'. The use of higher levels of initiators of the present invention can also be used but polymers of lower molecular weight are normally obtained when higher initiator levels are used. However, higher initiator levels can be used when carrying out the polymerizations at lower temperatures without sacrificing molecular weight.

Also, higher initiator levels are sometimes used to obtain shorter polymerization cycles. In any event, a variety of techniques can be employed to incorporate various levels of ultraviolet light stabilizing groups into the polymer or copolymer using the initiators of the present invention.

The novel free radical generators of the present invention can also be used to provide UV light stabilization to a variety of other materials which are prepared via processes requiring free radical generators. For example, they can be used as curing agents for resins such as alkyds and unsaturated polyester-vinyl monomer blends to provide the cured resins which are stabilized against UV light degradation. Unsaturated polyester resins that can be cured by the initiators of this invention usually consist of an unsaturated polyester and one or more polymerizable monomers. The unsaturated polyesters are, for instance, obtained by esterifying at least one ethylenically unsaturated di- or polycarboxylic acid, anhydride or acid halide, such as maleic acid, fumaric acid, glutaric acid, itaconic acid, mesaconic acid, citraconic acid, allylmalonic acid, allylsuccinic acid, tetrahydrophthalic acid and others with saturated or unsaturated di- or polyols, such as ethylene glycol, diethylene glycol, tri-ethylene glycol, 1,2- and 1,3-propanediols, 1,2-, 1,3- and 1,4-butanediols, 2,2-dimethyl-1,3-propanediol, 2-hydroxymethyl-2-methyl-1,3-propanediol, 2-buten-1,4-diol, 2-butyn-1,4-diol, 2,2,4-trimethyl-1,3-pentanediol, glycerol, pentaerythritol, mannitol and others. Mixtures of such polyacids and/or mixtures of such polyalcohols may also be used. The unsaturated di- or polycarboxylic acids may be replaced, at least partly, by saturated polycarboxylic acids, such as adipic acid, succinic acid, sebacic acid and others and/or by aromatic polycarboxylic acids, such as phthalic acid, trimellitic acid, pyromellitic acid, isophthalic acid and terephthalic acid. The acids used may be substituted by groups such as halogen. Examples of such suitable halogenated acids are, for instance, tetrachlorophthalic acid, 2,3-dicarboxy-1,4,5,6,7,7-hexachlorobicyclo(2.2.1)-2-heptene and others. The other component of the unsaturated polyester resin composition, the polymerizable monomer or monomers, can be preferably ethylenically unsaturated monomers, such as styrene, chlorostyrene, vinyltoluene, divinylbenzene, alpha-methylstyrene, diallyl maleate, di-allyl phthalate, dibutyl fumarate, acrylonitrile, triallyl phosphate, triallyl cyanurate, methyl acrylate, methyl methacrylate, n-butyl methacrylate, ethyl acrylate and others, or mixtures thereof, which are copolymerizable with said polyester. A preferred resin composition contains as the polyester component the esterification product of 1,2-propylene glycol (a polyalcohol), maleicanhydride (an anhydride of an unsaturated polycarboxylic acid) and phthalic anhydride (an anhydride of an aromatic dicarboxylic acid) as well as the monomer component, styrene. Temperatures of about 20° to 200° C and initiator levels of about 0.05% to 5% or more by weight of curable unsaturated polyester resin are normally employed.

The free radical generators of the instant invention can also be used as vulcanization agents for natural and synthetic rubbers and elastomers such as the silicone rubbers and the ethylene-propylene copolymers to provide vulcanized rubbers and elastomers which are stabilized against UV light degradation. They can also be used as crosslinking agents for various thermoplastic polymers and copolymers, such as polyethylene, poly-

propylene, ethylene-vinyl acetate copolymer, to provide the cross-linked polymers which are stabilized against UV light degradation. They can be used as the free radical sources for preparing block and graft copolymers to provide such copolymers which are stabilized against UV light degradation. Other uses for the novel free radical generators of the present invention to provide a source of free radicals and also impart stabilization toward UV light in the system will become apparent to those skilled in the art.

The novel free radical generators of this invention can be prepared by a variety of techniques such as:

1. reaction of a UV stabilizer having pendant OH, SH or NH groups (which are not necessary for UV absorption) with azos or peroxides containing acylating functions, as disclosed in copending application Ser. No. 667,352, filed Sept. 13, 1967, now abandoned with respect to azos and as disclosed in copending application Ser. No. 727,323, filed May 7, 1968, now U.S. Pat. No. 3,671,651, with respect to peroxides;

2. reaction of a UV stabilizer containing an acylating function with an azo or peroxide containing a reactive OH, SH or NH group;

3. rearrangement of azos or peroxides containing phenyl esters of carboxylic acids. The rearrangement can take place either prior to using the free radical generator or as a post reaction, usually during the processing of the final product (polymer). This rearrangement is known as the Fries Reaction and can occur under thermal, photo, or Friedel Crafts conditions;

4. reaction of a UV stabilizer containing an active halogen (e.g. from a chloromethylation reaction) with an azo or peroxide containing a carboxylic acid salt; and

5. reaction of an azo or peroxide containing an active halogen with a UV stabilizer containing a carboxylic acid salt.

The evaluation of the novel initiators for their ability to produce UV stabilized polymers has been determined by polymerizing styrene using certain of the novel initiators and then determining the retention of flexural strength of the polystyrene upon exposure to UV light. The retention of flexural strength according to a modified ASTM Procedure D790-63 was compared with the retention of flexural strength of polystyrene prepared from azo and peroxide initiators of similar structure which did not have UV absorbing groups on them. Comparisons were also made with a polystyrene in which an extraneous UV absorber had been added after the polymerization was complete. Table II describes the polymerization initiator, the parts of the initiator per 100 hundred parts of monomer, the UV absorber present, the hours of exposure to UV radiation, the flexural strength and the per cent flexural strength retained after UV exposure.

By comparing Runs 1-3 it is easy to see that the polystyrene prepared from the novel initiator 2-(4-t-butyl-azo-4-cyanovaleryloxy)-2-hydroxybenzophenone had the greatest retention of flexural strength. The polystyrene which was prepared by adding an extraneous UV absorber during the polymerization (Run 3) had intermediate stability with degradation occurring after 160 hours of UV radiation. The polystyrene without any UV stabilizer present (Run 2) had very poor stability, its flexural strength retention dropping to 57% after only 80 hours exposure.

By comparing Runs 4-6, it is again easy to see that the polystyrene prepared from the novel azo initiator (Run 4) had the greatest retention of flexural strength. In fact,

the flexural strength actually increased on prolonged radiation. Again the polystyrene which was prepared by adding an extraneous UV absorber during the polymerization (Run 6) had intermediate stability. The polystyrene without any UV stabilizer present (Run 5) had very poor stability again.

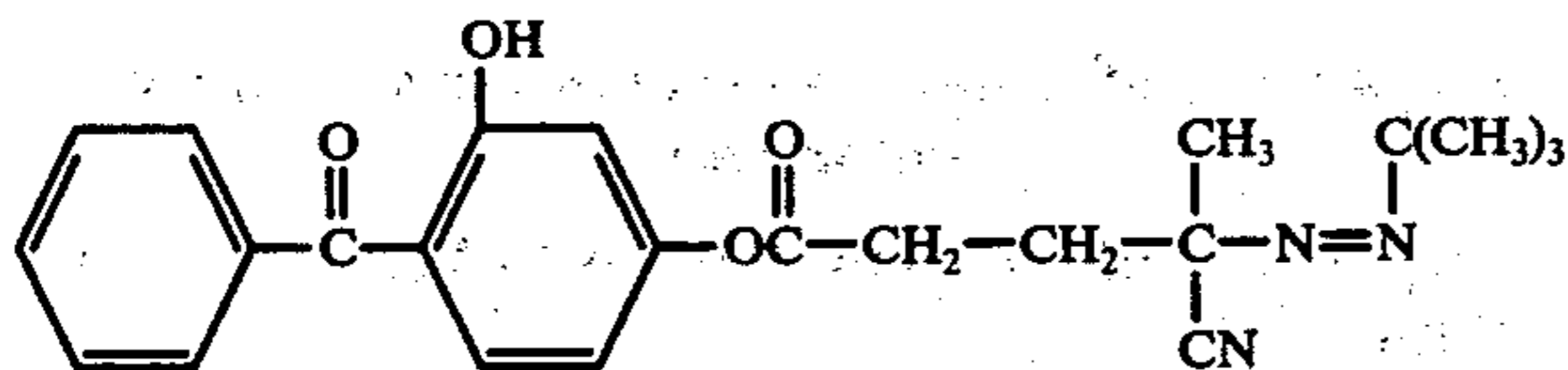
By comparing Runs 9-11, it is obvious that the novel peroxide initiators are also quite effective in stabilizing polystyrene against UV radiation. Again the polystyrene prepared from the novel initiator (Run 9) had the greatest retention of flexural strength. The polystyrene which was prepared by adding an extraneous UV absorber during the polymerization (Run 11) had intermediate stability and the polystyrene without any UV stabilizer present (Run 10) had very poor stability.

It should be noted that the molecular weights of the polymers obtained in Runs 7, 8 and 12 in which the UV absorber was added on the mill are much lower than comparable samples in which no UV absorber was added. This indicates that polymer degradation was occurring on the mill. Therefore, this is not a very desirable method of incorporating a UV absorber into a polymer. Due to the polymer degradation on the mill, these polymers were not subjected to the UV radiation. Adding an extraneous UV absorber during a polymerization is not a very desirable method of incorporating a UV absorber into a polymer either, since this foreign substance can very often change the rate, and/or degree of polymerization as well as the molecular weight and physical properties of the finished polymer. It can also be partly or completely removed from the polymer in those instances where the polymer must be purified by washing and extraction techniques or during the removal of the medium used for the polymerization.

In the following examples, there are presented illustrative embodiments of this invention. Percentages and parts are by weight, and temperatures are in degrees centigrade unless otherwise noted.

#### EXAMPLE IA

##### Preparation of 4-(4-t-Butylazo-4-cyanovaleryloxy)-2-hydroxybenzophenone



To a solution of 4.7 g. (.022 m) of 2,4-dihydroxybenzophenone and 2.5 ml. of pyridine in 35 ml. of ether in a 4 neck 100 ml. round bottom flask containing a thermometer, condenser and magnetic stirring bar was added 4.0 g. (.0218 m) of 4-t-butylazo-4-cyanovaleryl chloride dropwise with cooling so the temperature did not rise above 25° C. After completion of the addition the reaction mixture was stirred ½ hour at room temperature and then diluted with 100 ml. of water. The ether layer was separated, washed consecutively with 5% HCl, water, and 10% NaHCO<sub>3</sub> solution and saturated sodium chloride solution. The ether was evaporated off and the residue dissolved in methylene chloride, dried over anhydrous sodium sulfate, filtered and the methylene chloride stripped off under reduced pressure. The product weighed 8.8 g. (99% yield) and was a viscous

syrup. The infrared spectrum was in agreement with the structure of the desired product.

#### Preparation of 4-t-Butylazo-4-cyanovaleryl chloride.

##### A. Preparation of 4-t-butylazo-4-cyanovaleric acid.

To a mixture of 10.2 grams (.0876 mole) of levulinic acid in 25 ml of water was added in the following sequence: 7.04 grams (.0876 mole) of 50% sodium hydroxide, 5.88 grams (.12 mole) of sodium cyanide and 10.9 grams (.0438 mole) of t-butylhydrazine hydrochloride. The reaction mixture was stirred for 5 hours at room temperature, cooled to 5° C. and chlorine passed into the system holding the temperature below 15° C. until there was an increase in weight 10.0 grams (.14 mole).

After the chlorination was over, the product was extracted with methylene chloride, the methylene chloride solution washed twice with water, dried over anhydrous sodium sulfate, filtered, and the methylene chloride evaporated on a rotating evaporator to leave 9.70 grams (52.5% yield) of crude product. The crude material was recrystallized from benzene-pentane to give 8.0 grams of product having a melting range of 79°-81° C.

##### B. Preparation of 4-t-butylazo-4-cyanovaleryl chloride.

Into a 25 ml round bottom flask was weighed 5 grams (.0237 mole) of 4-t-butylazo-4-cyanovaleric acid and then 15 ml of benzene and 2 ml of thionyl chloride were added. The acid dissolved and the solution was stirred for 4 hours at 25° ± 2° C (protected from the atmosphere by a CaCl<sub>2</sub> tube). At the end of the stirring period the benzene and excess leaving 5.35 grams (98.8% yield) of 4-t-butylazo-4-cyanovaleryl chloride.

#### EXAMPLE IB

##### Curing an Unsaturated Polyester-Styrene Resin with 4-(4-t-butyl-azo-4-cyanovaleryloxy)-2-hydroxybenzophenone

An unsaturated polyester resin was prepared by reacting maleic anhydride (1.0 mole), phthalic anhydride (1.0 mole), and propylene glycol (2.2 moles) until an acid number of 45-50 was obtained. To this was added hydroquinone at a 0.013% concentration. Seven parts of this unsaturated polyester was diluted with 3 parts of monomeric styrene to obtain a homogeneous blend

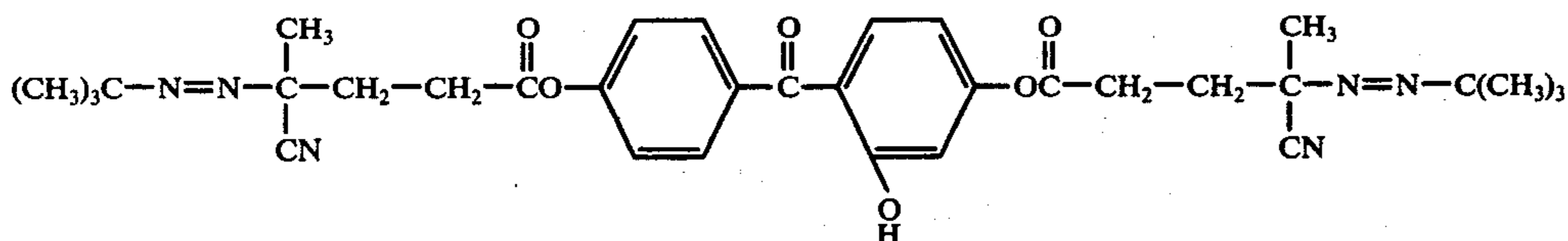
having a viscosity of 13.08 poise and a specific gravity of 1.14.

To 20 grams of this blend was added 0.2 gram of 4-(4-t-butylazo-4-cyanovaleryloxy)-2-hydroxybenzophenone and the resultant composition placed in a constant temperature bath at 212° F. The internal temperature was recorded as a function of time and a peak exotherm of 422° F was reached in 6.6 minutes indicating an excellent cure of the unsaturated polyester-styrene resin blend had occurred. Without an initiator, no cure of this blend occurred after more than 30 minutes at 212° F.



## EXAMPLE II

Preparation of  
4,4'-Di(4-t-butylazo-4-cyanovaleryloxy)-2-hydroxybenzophenone

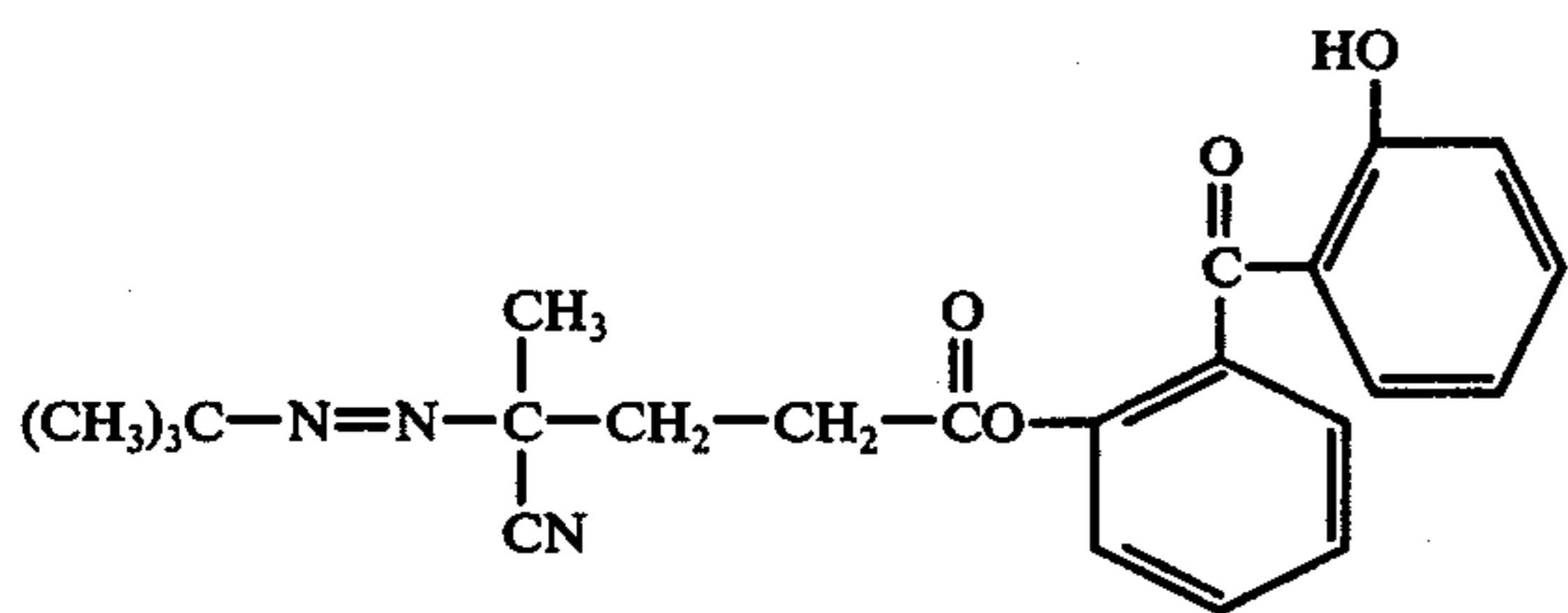


To a solution of 2.04 g. (.0085 m) of 2,4,4'-trihydroxybenzophenone and 2.5 ml of pyridine in 30 ml of ether in a 4 neck 100 ml round bottom flask equipped with a thermometer, condenser and magnetic stirring bar was added 3.9 g. (.017 m) of 4-t-butylazo-4-cyanovaleryl

chloride dropwise with cooling so the temperature did not rise about 25° C. After completion of the addition the reaction mixture was stirred ½ hour at room temperature and then diluted with 100 ml of water. The ether layer was separated, washed consecutively with 5% HCl, water, 10% NaHCO<sub>3</sub> solution and saturated sodium chloride solution. The ether was evaporated off and the residue dissolved in methylene chloride, dried over anhydrous sodium sulfate, filtered and the methylene chloride stripped off under reduced pressure. The product weighed 4.0 g. (77% yield) and was a viscous syrup. The infrared spectrum of the product was in agreement with the structure of the desired product.

## EXAMPLE III

Preparation of  
2-(4-t-butylazo-4-cyanovaleryloxy)-2'-hydroxybenzophenone

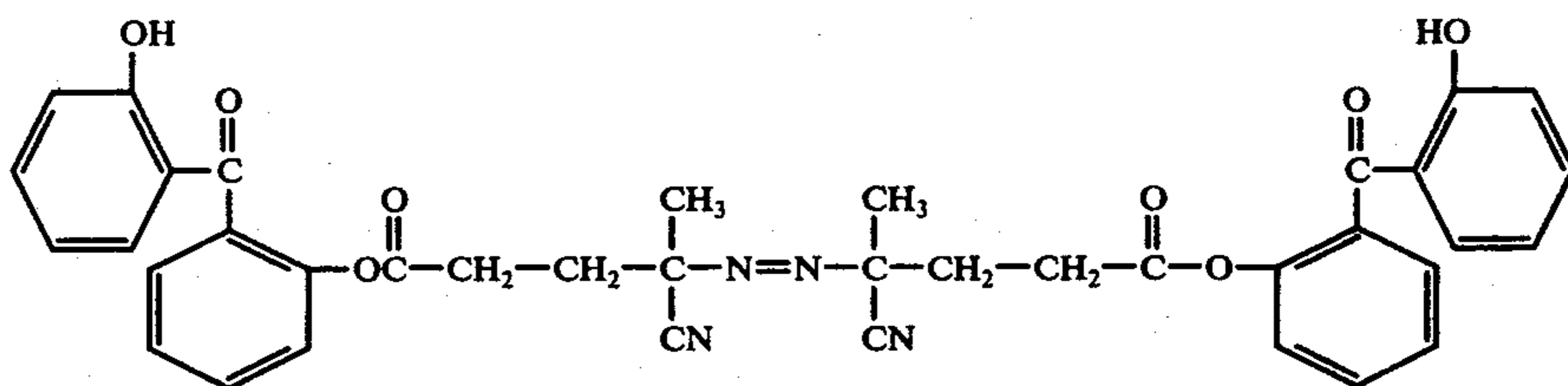


To a solution of 4.68 g. (.0218 m) of 2,2'-dihydroxybenzophenone and 2.5 ml of pyridine in 30 ml of ether in a 4 neck 100 ml round bottom flask equipped with a thermometer, condenser and magnetic stirring bar was added 5.0 g. (0.0218 m) of 4-t-butylazo-4-cyanovaleryl chloride dropwise with cooling so the temperature did not rise above 25° C. After completion of the addition the reaction mixture was stirred ½ hour at room temperature and then diluted with 100 ml of water. The ether layer was separated, washed consecutively with 5% HCl, water, 10% NaHCO<sub>3</sub> solution and saturated sodium chloride solution. The ether was evaporated off

leaving a yellow solid. The solid was slurried in pentane, filtered and air dried. The product weighed 6.3 g. (71.2% yield) and decomposed slowly on heating above 80° C. The infrared spectrum of the product was in agreement with the structure of the desired product.

## EXAMPLE IV

PREPARATION OF  
Di-[2-(2-hydroxybenzoyl)phenyl]  
trans-4,4'-azobis(4-cyanovalerate)



To a solution of 7.05 g. (.0328 m) of 2,2'-dihydroxybenzophenone and 3.5 ml. of pyridine in 50 ml. of benzene in a 4 neck 100 ml round bottom flask equipped with a thermometer, condenser and magnetic stirring bar was added 5.2 g. (.0164 m) of trans-4,4'-azobis(4-cyanovaleryl chloride) as a solid in small increments with cooling so the temperature did not rise above 25° C. After completion of the addition the reaction mixture was stirred 2 hours at room temperature and then diluted with 100 ml of water. The benzene layer was separated and washed with 5% HCl and water. It was dried over anhydrous sodium sulfate, filtered and the benzene stripped off. The product was a viscous syrup and weighed 8.4 g. (76% yield). The infrared spectrum of the product was in agreement with the structure of the desired product.

## Preparation of Trans-4,4'-Azobis(4-cyanovaleryl chlorides)

## A. Preparation of Cis- and Trans-4,4'-Azobis(4-cyanovaleric acid)

A solution of 154.8 grams (1.32 moles) levulinic acid, 53.2 grams (1.32 moles) sodium hydroxide and 21.8 grams (0.66 mole) of 97% hydrazine was refluxed in an oil bath for 5 hours. The solution was cooled to room temperature, 160 ml HCN added, and the reaction stirred overnight. The solution was then made acid with a few ml of conc. HCl and the excess HCN was stripped off under aspirator vacuum, trapping the volatile HCN in "Dry Ice" trap. After most of the excess HCN had been stripped off, the solution was made basic again with 50% NaOH and chlorine passed into the system. The temperature was controlled below 15° C by means of an ice bath and the chlorine passed in until the exotherm ceased (approximately 85 grams or 1.2 moles). During the oxidation, a solid precipitated out of solution. The solid was filtered off, washed once with cold water and air dried. The crude yield was 140 grams (76% yield) of a light brown powder having a melting

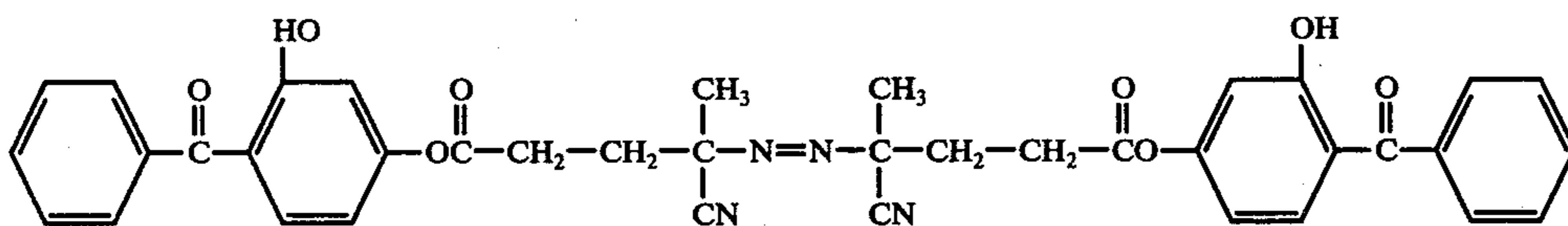
range of 118°–125° C. Repeated recrystallization from ethyl alcohol and ethyl acetate separated the product into two pure isomeric forms, one melting at 141°–143° C (35 grams from ethanol) and the other at 125°–127° C (22.5 grams from ethyl acetate). The higher melting isomer was also the less soluble isomer and was assigned the trans-structure, and the other isomer was assigned the cis-structure.

**B. Preparation of Trans-4,4'-azobis(4-cyanovaleryl chloride)**

A mixture of 10 grams (0.0358 mole) trans-4,4'-azobis(4-cyanovaleric acid) and 200 ml of thionyl chloride in a 500 ml round bottom flask containing a magnetic stirring bar and a condenser with a drying tube, was refluxed for 1 hour in a 100° C oil bath. The resulting solution was filtered while still warm and the excess thionyl chloride stripped from the filtrate. The residue was slurried in benzene and stripped to dryness. The resultant solid was dissolved in warm benzene, filtered and precipitated back out with pentane. The solid was filtered off and dried. The yield was 5.4 grams (47.5% yield) of a white powder with a melting range of 81°–83° C. (dec.).

**EXAMPLE V**

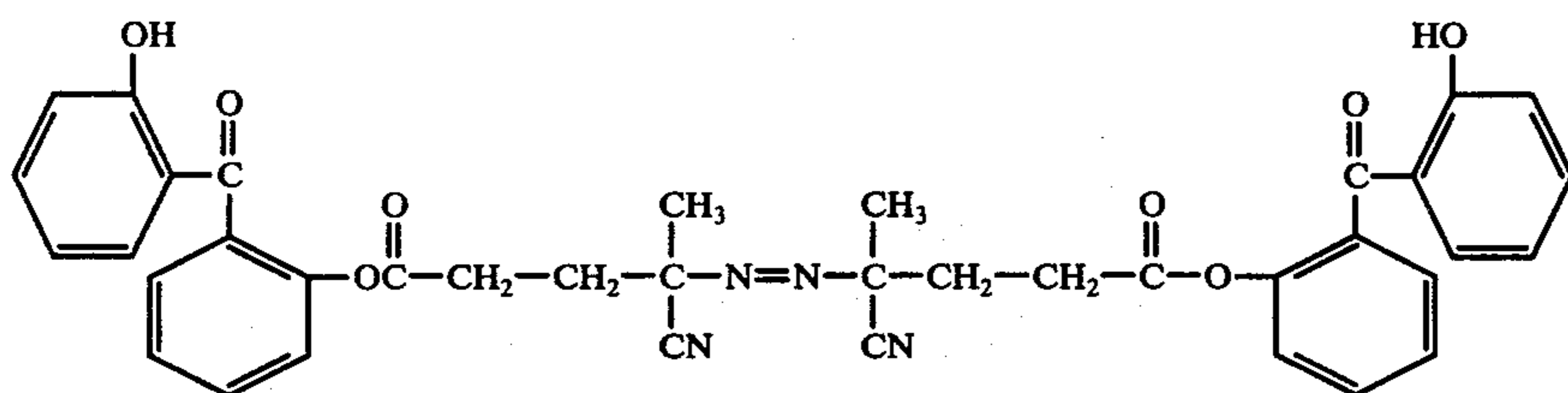
**Preparation of Di-(3-hydroxy-4-benzoylphenyl)trans-4,4'-azobis(4-cyanovalerate)**



To a solution of 10.7 g. (0.050 m) of 2,4-dihydroxybenzophenone and 4.5 ml. of pyridine in 70 ml. of methylene chloride in a 200 ml. 4-neck round bottom flask equipped with a thermometer, condenser and magnetic stirring bar was added 7.9 g. (0.025 m) of trans-4,4'-azobis(4-cyanovaleryl chloride) as a solid in small increments with cooling so the temperature did not rise above 25° C. After completion of the addition the reaction mixture was diluted with 150 ml. water and the methylene chloride layer separated. The organic layer was washed with 5% HCl and water, dried over anhydrous sodium sulfate, filtered and the methylene chloride stripped off. The residue was a light tan tacky solid weighing 15.2 g. (90.5% yield). The infrared spectrum of the product was in agreement with the structure of the desired product.

**EXAMPLE VI**

**Preparation of Di-[2-(2-hydroxybenzoyl)phenyl]cis-4,4'-azobis(4-cyanovalerate)**



To a solution of 12.5 g. (0.0583 m) of 2,2'-dihydroxybenzophenone and 6 ml. of pyridine in 75 ml. of benzene in a 4 neck 200 ml. round bottom flask equipped

with a thermometer, condenser and magnetic stirring bar was added 9.2 g. (0.0291 m) of cis-4,4'-azobis(4-cyanovaleryl chloride), as a solid in small increments, with cooling so the temperature did not rise above 35° C. After completion of the addition, the reaction mixture was stirred 2½ hours at room temperature and then diluted with 100 ml. water. The benzene layer was separated and washed with 5% HCl and then with water until neutral. The benzene solution was dried over anhydrous sodium sulfate, filtered and the benzene stripped off. The residue was a light yellow tacky solid weighing 20.5 g. (105% yield). The infrared spectrum showed the product was in agreement with the structure of the desired product and that a small amount of benzene was still present in the tacky solid.

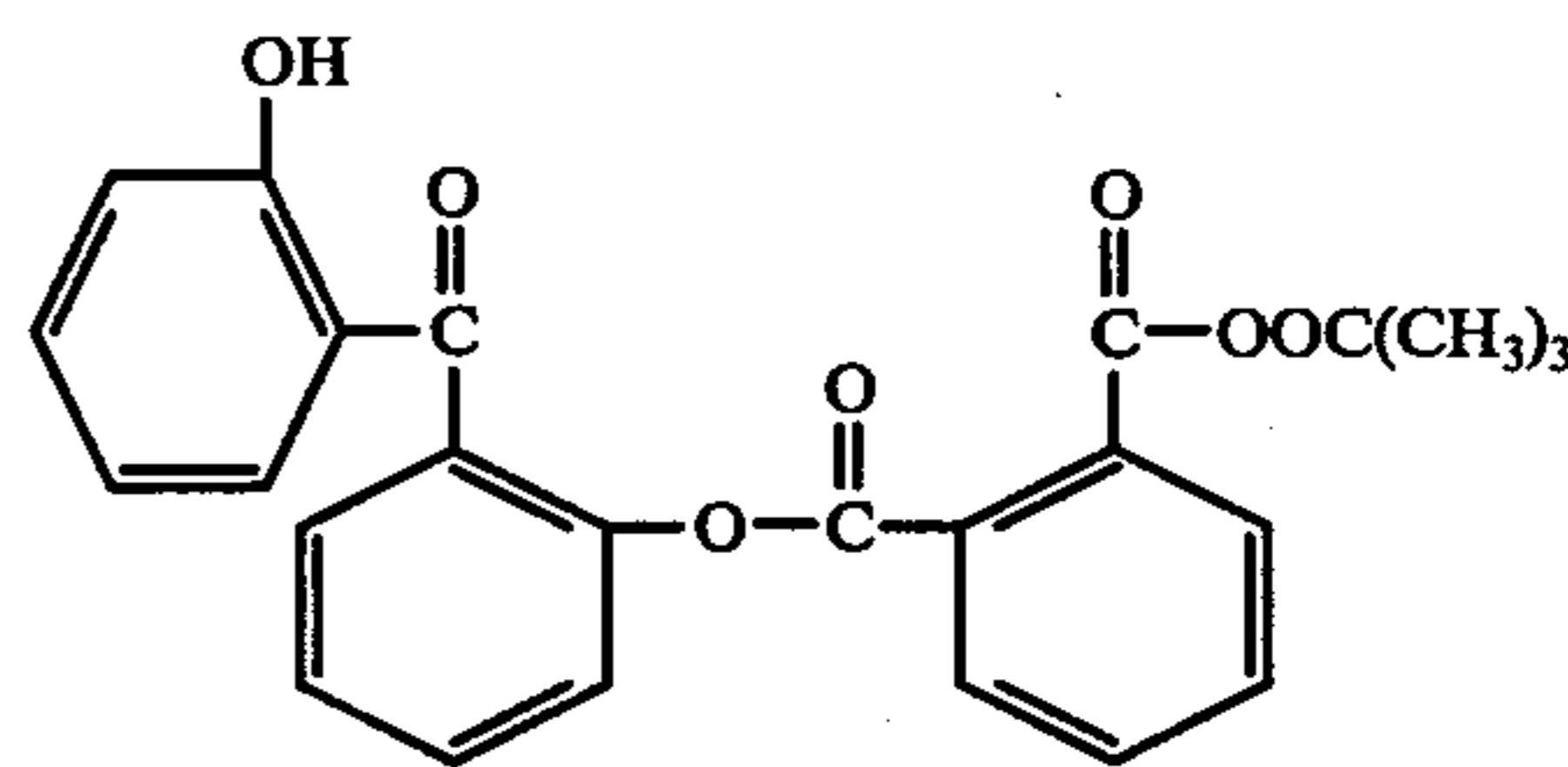
**Preparation of Cis-4,4'-Azobis(4-cyanovaleryl chloride)**

A 500 ml. 3-neck flask containing 20.7 grams (0.074 mole) of cis-4,4'-azobis(4-cyanovaleric acid) (prepared as described in Example IV), 120 ml. thionyl chloride, a magnetic stirring bar, a thermometer, and a condenser with a drying tube was immersed into an oil bath preheated to 125° C. At the end of 8 minutes complete solution was obtained and the oil bath was rapidly replaced by an ice bath. The solution was cooled to room temperature and the excess thionyl chloride stripped off. The residue was slurried in benzene and the benzene stripped off. The resulting solid was dissolved in warm

benzene and then precipitated by the addition of pentane. The precipitate was filtered off and dried. The yield was 20.7 grams (88.4% yield) of a white powder with a melting range of 88°–90° C. (dec.).

**EXAMPLE VII**

**Preparation of 00-t-butyl 0-2-(2-hydroxybenzoyl)phenyl monoperoxyphthalate**



To a solution of 10.7 g. (.05 m) of 2,2'-dihydroxybenzophenone and 4.9 ml of pyridine in 50 ml. of methylene

chloride in a 4 neck 100 ml. round bottom flask equipped with a thermometer condenser and magnetic

stirring bar was added 12.8 g. (.05 m) of t-butyl peroxy-2-(chloro-carbonyl) benzoate dropwise over  $\frac{1}{2}$  hour holding the temperature between 20°–25° C with a cold water bath. After the addition was complete, the reaction mixture was stirred an additional 1 hour at room temperature. The reaction was then diluted with 100 ml of water, the methylene chloride layer separated and washed consecutively with 5% HCl, water, 10% NaHCO<sub>3</sub> solution and saturated sodium chloride solution, dried over anhydrous sodium sulfate, filtered and the methylene chloride stripped off. The residue weighed 20.5 g. (94.3% yield) and assayed 85.6%. The infrared spectrum of the product was in agreement with the structure of the desired product.

Preparation of t-Butylperoxy  
2-(Chlorocarbonyl)benzoate

To a suspension of 22.9 grams (0.096 mole) OO-t-butyl hydrogen monoperoxyphthalate in 150 ml. of benzene at 10° C. was added 20.0 grams (0.096 mole) of PCl<sub>5</sub> in a single portion. The components went into solution, the ice bath was removed and the temperature was allowed to rise to room temperature. At the end of 1 $\frac{3}{4}$  hours stirring time, the reaction mixture was stirred into 150 ml. of ice water, stirred 3 minutes, the organic layer separated, dried over anhydrous sodium sulfate, filtered and the benzene evaporated under reduced pressure to give 23.5 grams (95.7% yield) of crude product. This

general process is described in copending patent application Ser. No. 727,323, filed May 7, 1968.

EXAMPLE VIII

General Procedure for Evaluation of UV Light Stability of Polystyrene Prepared from Novel Initiators

The polystyrene was prepared by a suspension polymerization technique using 1,000 grams of water, 0.0828 grams of gelatin, 50 grams of calcium phosphate, 500 grams of styrene and the amount of initiator indicated in Table II. In some cases, 2-acetoxy-2'-hydroxybenzophenone, a UV absorber of similar structure to that in the novel initiators used, was added during the polymerization step or after the polymerization on a rubber mill. In all cases, with the exception of the blanks, the concentration of the UV absorbing structure was kept at 0.5 parts per hundred of styrene monomer. The polymerizations were carried out between 75° – 95° C depending on the half-life of the initiator. In any event, the controls were run through the same heating cycle as the comparative polymerizations.

The polystyrene was press molded at 300° F for 5 minutes into 5 inches  $\times$   $\frac{1}{2}$  inch  $\times$   $\frac{1}{4}$  inch bars. These bars, four to a set, were then exposed to a Westinghouse 275 Watt sunlight bulb for 0, 80, 160, and 240 hours according to a modified ASTM Procedure D629-57T. After the exposure periods, flexural strengths of the polystyrene prepared from the various initiator systems were determined according to ASTM Procedure D790-63. The results are tabulated in Table II.

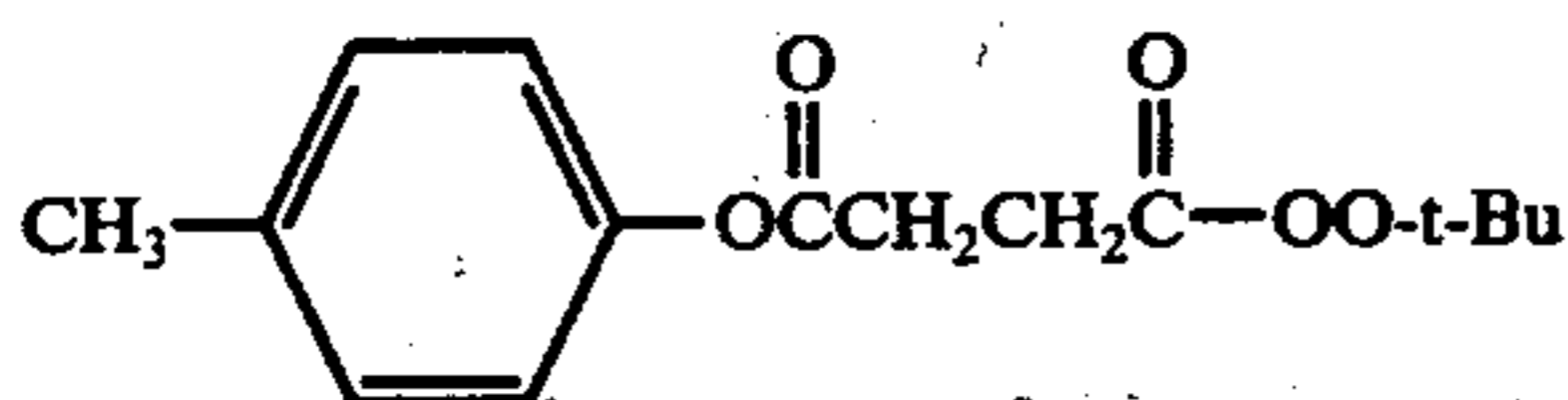
Run No.	Polymerization Initiator	M.W.	PHR	U.V. Absorber	PER of U.V. Absorber	Exposure to U.V. Radiation (Hours)	Flexural Strength (PDI)	% Flexural Strength Retained	Molecular Weight of Polymer
1	2-(4-t-Butylazo-4-cyanovaleryloxy)-2'-hydroxybenzophenone (From Example IA)	4C7	0.755	Attached	0.5	0 80 160 240	7243 6384 6595 6581	— 88.1 91.1 90.9	302,800
2	Ethyl 4-t-Butylazo-4-cyanovalerate	239	0.443	None	0	0 80 160 240	8708 4805 5088 4020	— 57.2 58.4 46.2	327,000
3	Ethyl 4-t-Butylazo-4-cyanovalerate	239	0.443	2-Acetoxy-2'-hydroxybenzophenone (added during polymerization)	0.5	0 80 160 240	6830 6328 6565 5053	— 92.7 96.1 74.0	333,000
4	Di-2-(2-hydroxybenzoyl)phenyl cis-4,4'-Azobis(4-cyanovalerate) (From Example VI)	672	0.624	Attached	0.5	0 80 160 240	5188 5100 5658 5615	— 98.3 108.2	314,500
5	Azobisisobutyronitrile	164	0.344	None	0	0 80 160 240	7626 6387 5715 3994	— 83.8 74.9 52.4	314,500
6	Azobisisobutyronitrile	164	0.344	2-Acetoxy-2'-hydroxybenzophenone (added during polymerization)	0.5	0 80 160 240	7173 6340 6750 6498	— 88.4 94.1 90.6	308,000
7	Ethyl 4-t-Butylazo-4-cyanovalerate	239	0.443	2-Acetoxy-2'-hydroxybenzophenone (added on mill)	0.5	0	6678	—	222,000
8	Azobisisobutyronitrile	8	0.344	2-Acetoxy-2'-hydroxybenzophenone (added on mill)	0.5	0	6600	—	167,800
9	OO-t-Butyl)-2-(2-Hydroxybenzoyl)-phenyl Monoperoxyphthalate	434	0.805	Attached	0.5	0 80	11023 10733	— 97.2	248,000

-continued

Run No.	Polymerization Initiator	M.W.	PHR	U.V. Absorber	PER of U.V. Absorber	Exposure to U.V. Radiation (Hours)	Flexural Strength (PDI)	% Flexural Strength Retained	Molecular Weight of Polymer
	(From Example VII)					160	9695	87.2	
						240	9783	87.7	
10	OO-t-Butyl O-Ethyl Monoperoxyphthalate	266	0.492	None	0.5	0	11830	—	248,000
						80	8595	72.6	
						160	7556	64.8	
						240	5721	48.4	
11	OO-t-Butyl O-Ethyl Monoperoxyphthalate	266	0.492	2-Acetoxy-2'-hydroxy-benzophenone (added during polymerization)	0.5	0	8814	—	213,000
						80	8578	97.3	
						160	7201	81.8	
						240	7200	81.8	
12	OO-t-Butyl O-Ethyl Monoperoxyphthalate	266	0.492	2-Acetoxy-2'-hydroxy-benzophenone (added on mill)	0.5	0	8691	—	174,000

## EXAMPLE IX

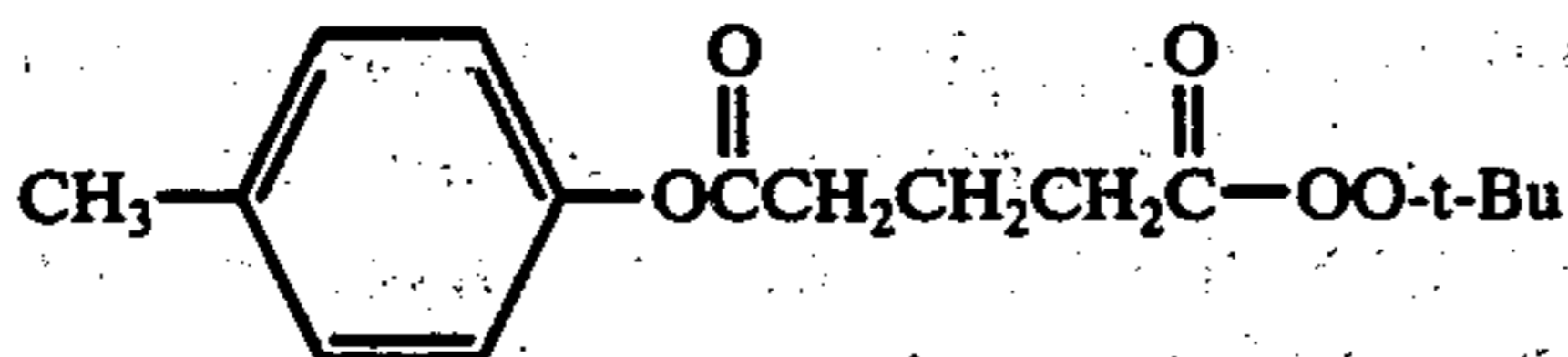
## Preparation of OO-t-Butyl O-p-Tolyl Monoperoxy succinate



To a vigorously stirred solution of 15.6 g. (0.143 mole) of 82.0% t-butyl hydroperoxide and 57.0 g (0.143 mole) of aqueous 10% sodium hydroxide at 5°-10° C was added slowly 24.6 g. (0.109 mole) of 3-(p-tolyloxycarbonyl)propionyl chloride (prepared from p-tolyl 3-carboxypropionate and thionyl chloride) in 50 ml. of diethyl ether. The reaction mixture was then stirred at 5°-10° C for three hours, after which additional ether was added to the mixture and the resulting ether solution was washed, first with 10% sodium hydroxide solution, and finally with water until the solution was neutral. After drying over anhydrous MgSO<sub>4</sub> and removal of the ether in vacuo 28.2 g. (theory, 30.4 g.) of white solid, m.p. 72°-77° C, was obtained. The assay according to "active oxygen" content was 100% and the corrected yield was 92.8%.

## EXAMPLE X

## Preparation of OO-t-Butyl O-p-Tolyl Monoperoxyglutarate

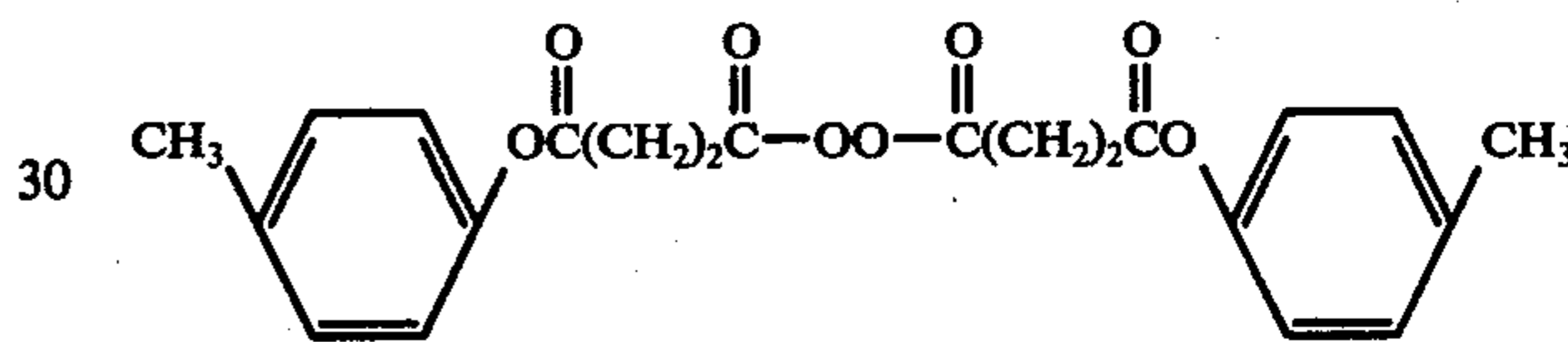


To a vigorously stirred solution of 4.9 g. (0.045 mole) of 82.0% t-butyl hydroperoxide and 18.0 g. (0.045 mole) of aqueous 10% sodium hydroxide at 10°-14° C was slowly added 8.2 g. (0.034 mole) of 4-(p-tolyloxycarbonyl)butyryl chloride (prepared from p-tolyl 4-carboxybutyrate and thionyl chloride) in 25 ml. of diethyl ether. The reaction mixture was then stirred for 3.5 hours at 8°-10° C. After a work-up similar to that in Example I 8.2 g. (theory, 10.0 g.) of white solid, m.p. 50°-55° C, was obtained. The assay according to "ac-

tive oxygen" content was 93.6% and the corrected yield was 76.7%.

## EXAMPLE XI

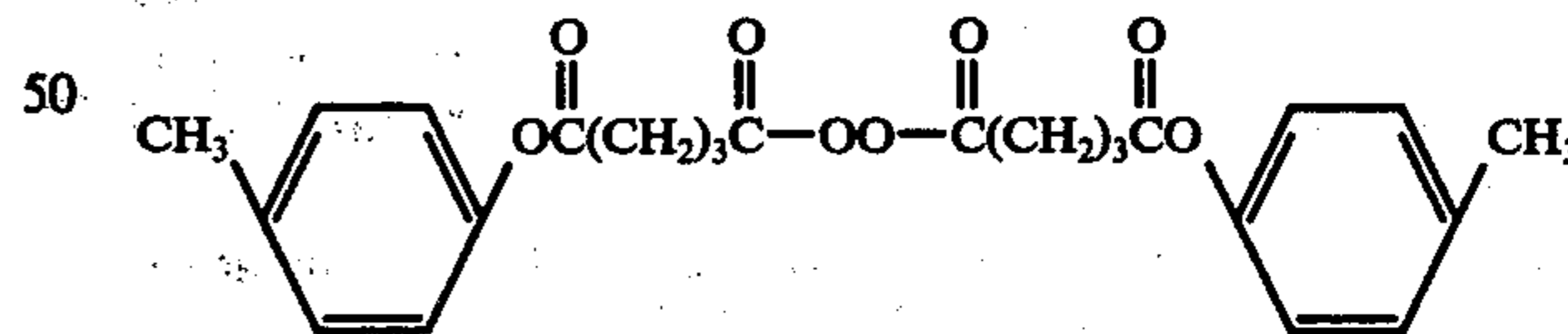
## 25 Preparation of Di-[3-(p-tolyloxycarbonyl)propionyl] Peroxide



To a vigorously stirred solution of 2.0 g. (0.029 mole) of 50% H<sub>2</sub>O<sub>2</sub> and 25.2 g. (0.063 mole) of aqueous 10% sodium hydroxide at 10°-14° C was added slowly 10.9 g. (0.0483 mole) of 3-(p-tolyloxycarbonyl)propionyl chloride in ether solution. The resulting reaction mixture was stirred for an additional three hours. After a work-up similar to that in Example I 9.1 g. (theory, 10.0g.) of white solid, m.p. 94°-106° C (decomp.) was obtained. The assay according to "active oxygen" content was 92.3% and the corrected yield was 83.9%.

## EXAMPLE XII

## Preparation of Di-[4-(P-tolyloxycarbonyl)butyryl] Peroxide



To a vigorously stirred solution of 1.7 g. (0.025 mole) of 50% hydrogen peroxide and 22.7 g. (0.057 mole) of aqueous 10% sodium hydroxide at 10°-14° C was slowly added a solution of 4-(p-tolyloxycarbonyl)butyryl chloride in 50 ml. of ether. The resulting reaction mixture was stirred for an additional three hours. After a work-up similar to that in Example I 7.5 g. (theory, 10.0 g.) of liquid was obtained. The assay according to "active oxygen" content was 81.5% and the corrected yield was 61.2%. After being stored at 0° C for several days the product solidified and had a melting point of 24°-30° C.

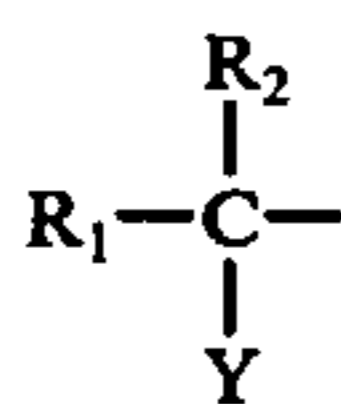
What is claimed is:

1. In the process of preparing a polymer containing an ultraviolet light stabilizer chemically bound to said polymer comprising polymerizing an ethylenically unsaturated monomer capable of being polymerized by free radicals in the presence of a free radical initiator the improvement comprising polymerizing said monomer in the presence of a free radical initiator containing ultraviolet light stabilizing groups and having the formula:

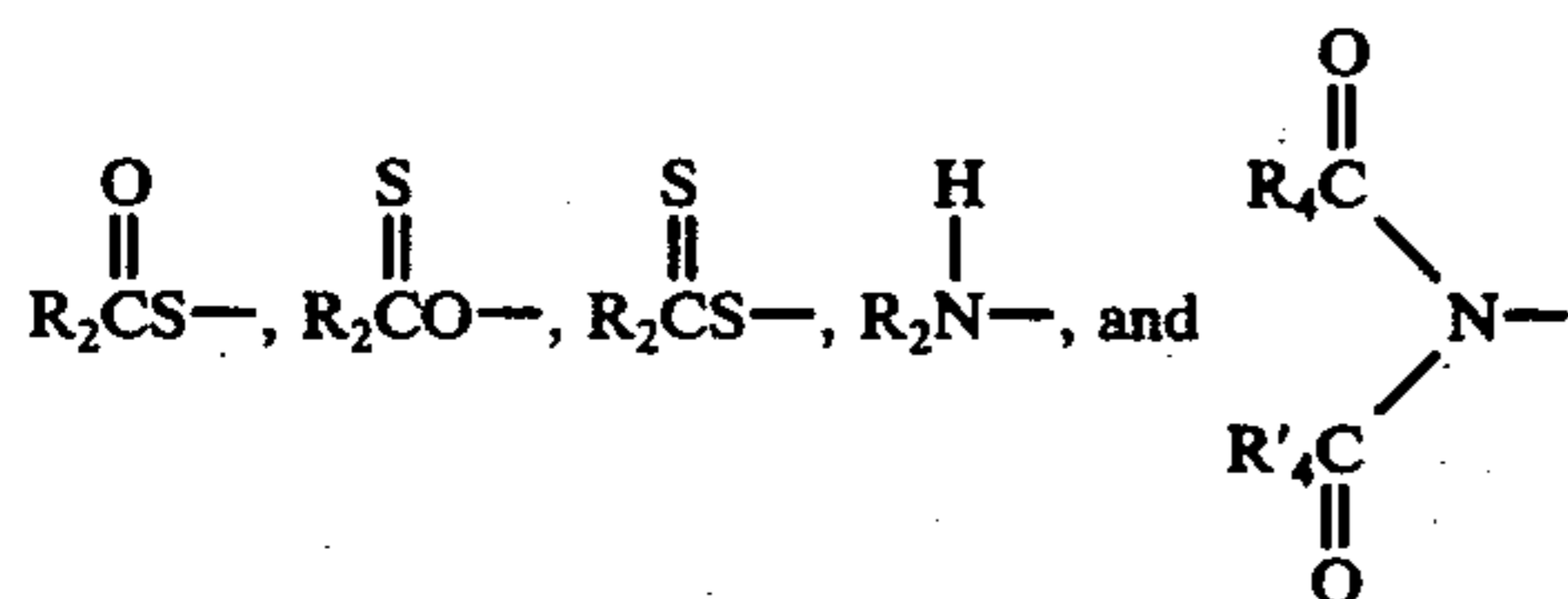
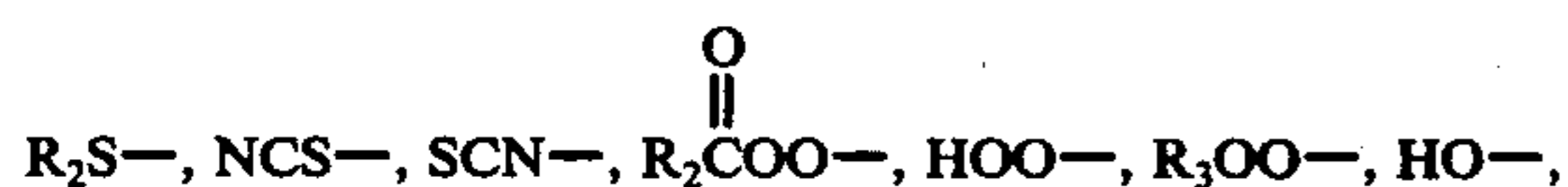
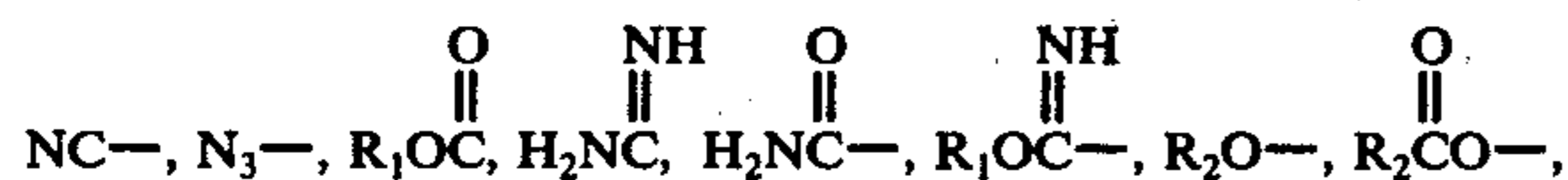


wherein

R' is selected from the group consisting of alkyl of 1-20 carbons, cycloalkyl of 3-10 carbons, aralkyl of 7-20 carbons and



wherein: Y is selected from the group consisting of



wherein

R<sub>1</sub> and R<sub>2</sub> are selected from the group consisting of alkyl of 1-20 carbons, cycloalkyl of 3-6 carbons, and alkylene of 2-30 carbons when R<sub>1</sub> and R<sub>2</sub> are joined together; and wherein one but not both of R<sub>1</sub> and R<sub>2</sub> may in addition be phenyl, tolyl, xylyl, benzyl, or phenethyl;

R<sub>3</sub> is t-alkyl of 4-8 carbons, t-cycloalkyl of 4-8 carbons or t-aralkyl of 9-15 carbons;

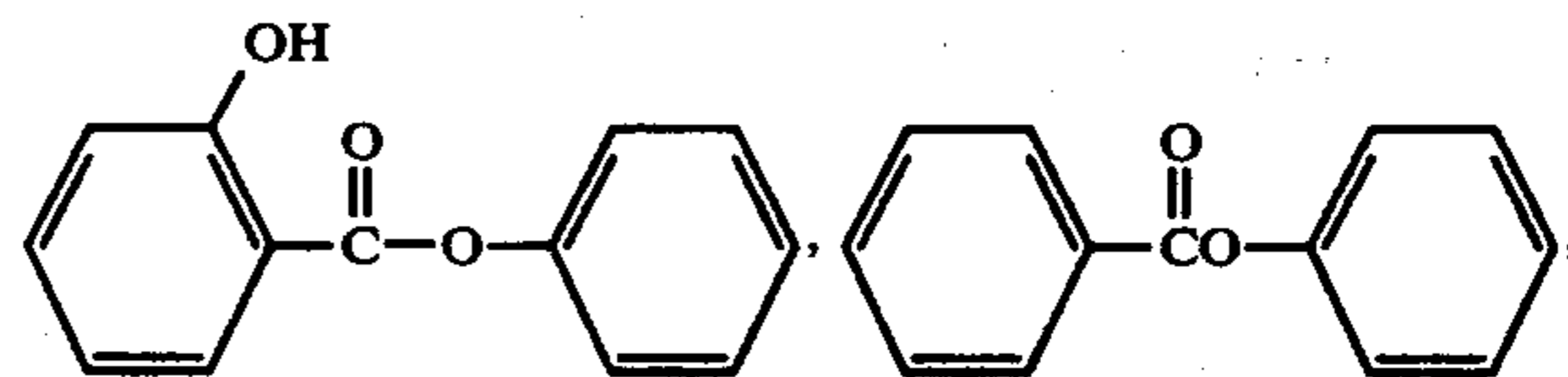
R<sub>4</sub> and R'<sub>4</sub> are alkyl of 1-6 carbons, cycloalkyl of 3-6 carbons or aryl of 6-12 carbons, when R<sub>4</sub> and R'<sub>4</sub> are joined together, and alkylene of 1-6 carbons or arylene of 6-12 carbons when R<sub>4</sub> and R'<sub>4</sub> are joined together;

R is any of the foregoing radicals of R', and in addition, may be selected from the group consisting of aryl of 6-14 carbons, acyl of 2-20 carbons, aroyl of 7-20 carbons, carbamoyl, alkylcarbamoyl of 2-7 carbons, cycloalkylcarbamoyl of 4-11 carbons, -CO<sub>2</sub>NA, -CO<sub>2</sub>K, alkoxy-carbonyl of 2-7 car-

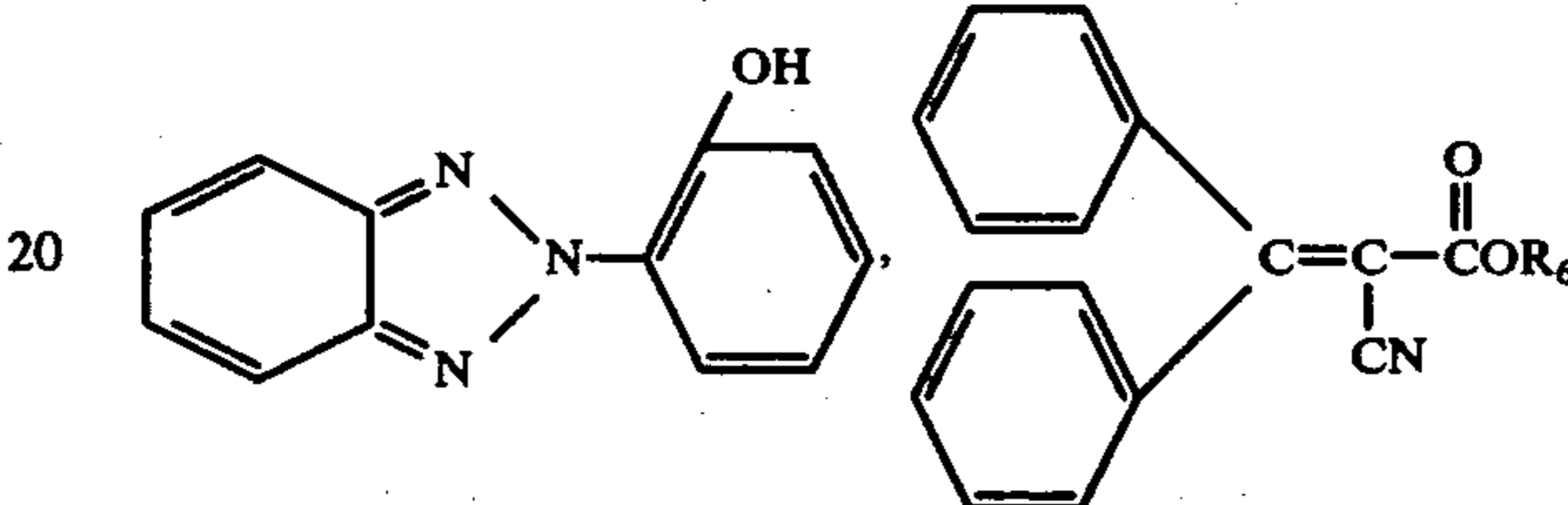
bons, cycloalkoxycarbonyl of 4-11 carbons, and aryloxy-carbonyl of 7-13 carbons, with the proviso that when R is carbamoyl, R' can be, in addition, alkoxy-carbonyl of 2-7 carbons, cycloalkoxycarbonyl of 4-11 carbons, or aryloxy-carbonyl of 4-11 carbons and

at least one of R and R' contains an ultraviolet light stabilizing radical of a compound selected from the group consisting of

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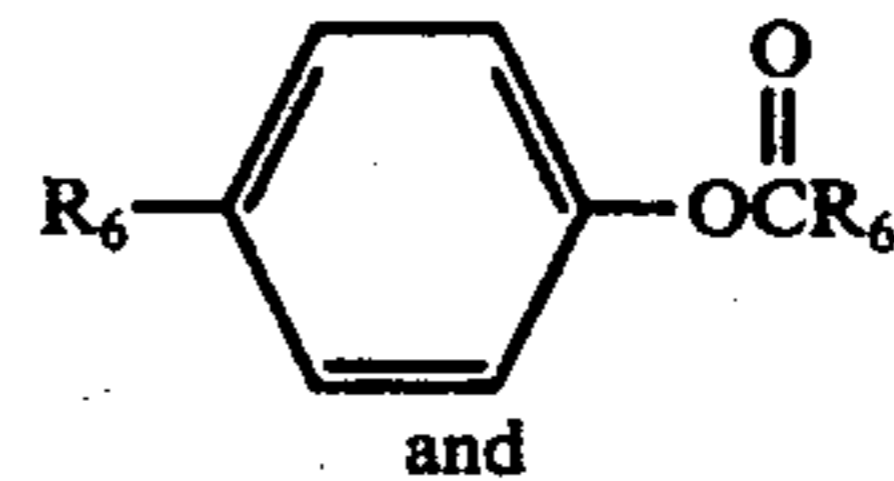


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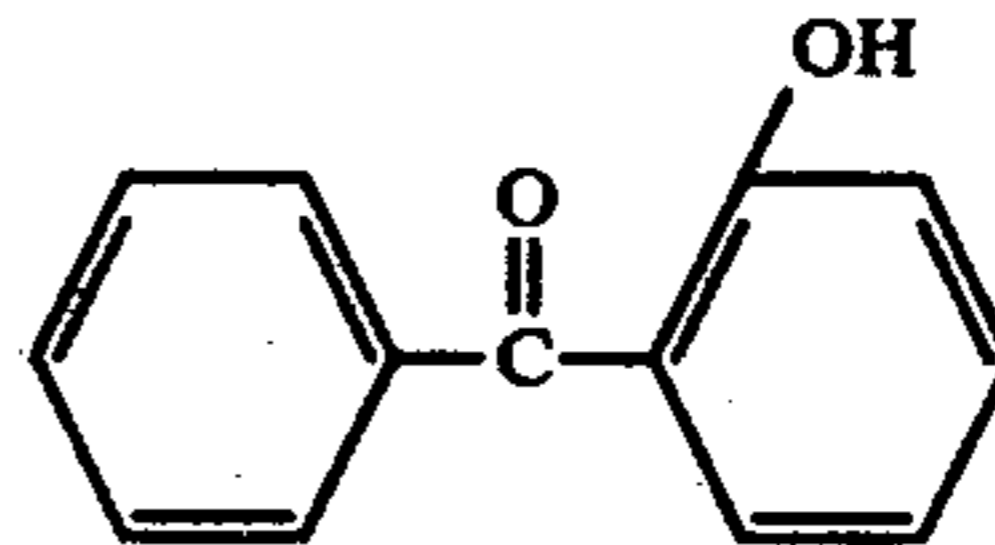
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and

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35 where R<sub>6</sub> is alkyl of 1-6 carbons.

2. The process of claim 1 wherein the monomer is styrene.

3. The process of claim 2 wherein the initiator is selected from 4-(4-t-butylazo-4-cyanovaleryloxy)-2-hydroxybenzophenone; 2-(4-t-butylazo-4-cyanovaleryloxy)-2'-hydroxybenzophenone; di-(2-(2-hydroxybenzoyl)phenyl) cis-4,4'-azobis(4-cyanovalerate) and di-(3-hydroxy-4-benzoylphenyl) trans-4,4'-azobis(4-cyanovalerate).

4. In the process of preparing a polymer containing an ultraviolet light stabilizer chemically bound to said polymer comprising polymerizing an ethylenically unsaturated monomer capable of being polymerized by free radicals in the presence of a free radical initiator the improvement comprising polymerizing said monomer in the presence of a free radical initiator containing ultraviolet light stabilizing group selected from 4-(4-t-butylazo-4-cyanovaleryloxy)-2'-hydroxybenzophenone; di-(2-(2-hydroxybenzoyl)phenyl) cis-4,4'-azobis(4-cyanovalerate); and di-3-hydroxy-4-benzoylphenyl)trans-4,4'-azobis(4-cyanovalerate).

\* \* \* \* \*

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